

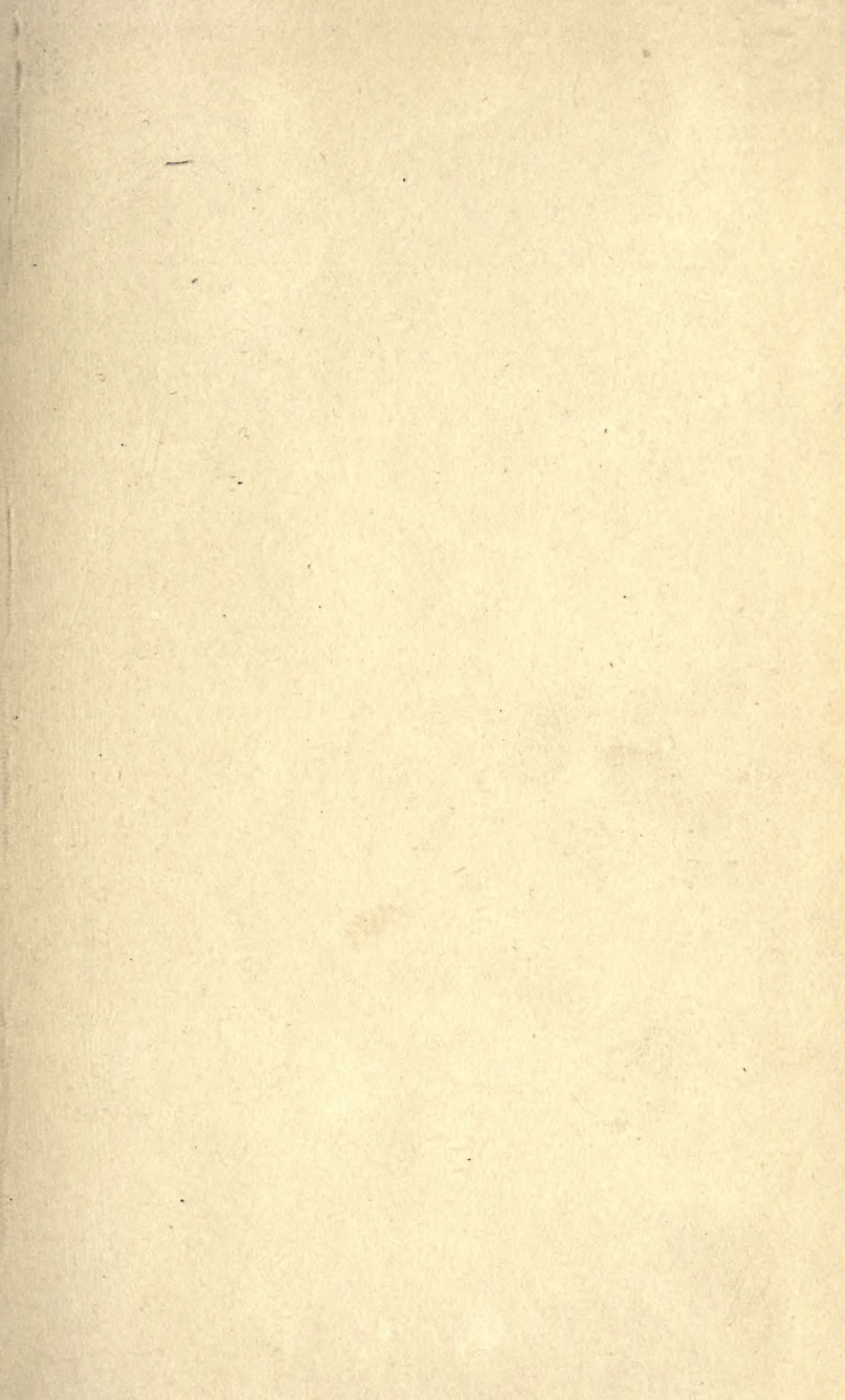


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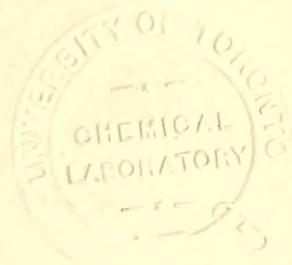






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**THE APPLICATION OF  
PHYSICO-CHEMICAL THEORY**





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# THE APPLICATION OF PHYSICO-CHEMICAL THEORY

TO TECHNICAL PROCESSES AND  
MANUFACTURING METHODS

BY  
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(GRAZ)

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## EDITOR'S PREFACE

THIS volume is one of the series of monographs on technical chemical methods of manufacture edited by Mr. L. Max Wohlgemuth. The books in this series have been written by experts with inside practical knowledge of their industries, and it is not remarkable that they have thus received a most encouraging reception in Germany. Indeed, surprise has been expressed that practical men should have proved so willing to give away so much of their special factory knowledge.

The series has not (with one exception) been introduced to English readers, and arrangements have therefore been made for the publication of a number of volumes particularly suited to the conditions of English industry. It seems fitting to begin with Prof. Kremann's valuable work, which has a comprehensive scope and should prove suggestive to chemists interested in many industries.

ALBERT MOND.



## AUTHOR'S PREFACE

PHYSICAL CHEMISTRY used to be considered a somewhat theoretical branch of study, but it has recently developed in such a way as to explain many of the empirical observations of technology and to prove extremely suggestive of many new methods. Such a tendency may be considered one of the highest aims of scientific research.

The young chemist frequently feels this in his first few terms, and I have found that of all the problems of physical chemistry the beginner shows most interest in those which have a bearing on technical questions. On this account, for some years now I have devoted a special section of my main course on physical chemistry to "The application of physico-chemical theories to technical problems."

The editor and publisher of this series recognise the great importance of physical chemistry in chemical technology, and I am much indebted to them for the readiness with which they have acceded to my desire to publish my lectures in this series, "The methods of manufacture of chemical technology." This volume of the series is to some extent a resumé of physico-chemical theories as applied to technical problems, which it is hoped will meet the requirements of chemists engaged in practice, as well as of students.

Electro-chemical questions have been purposely omitted, but for the sake of completeness a number of fundamental subjects have been briefly considered, e.g. the theory of the blast furnace,



portland cement, etc., although these are treated in separate monographs. As I have said, my object is to provide the reader with a connected picture of the application and significance of the various physico-chemical theories in technical problems, since these applications are only to be found elsewhere either in monographs or scattered throughout the technical literature. It is hoped that the book will fulfil its object by affording a stimulus to practical chemists, and a useful aid to students.

THE AUTHOR

GRAZ, *March*, 1911

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# Application of Physico-Chemical Theory to Manufacturing Processes

## CHAPTER I

### THE TWO FUNDAMENTAL LAWS OF THE MECHANICAL THEORY OF HEAT

#### **1. The First Fundamental Law. The Direct Determination of the Calorific Value of Fuels.**

NUMEROUS fruitless attempts have been made to discover perpetual motion, i.e. to invent a machine which can go on furnishing external work for ever. We have become convinced that such a machine is impossible and that the conception which underlies its construction must be in opposition to a natural law. If we subject any system to a cyclical process, i.e. if we subject it to any changes, and finally bring it back to the initial state again, we find that the external work  $A$  performed by the system during the cyclical process is proportional to the quantity of heat  $W$  which is absorbed, and we have

$$A = JW.$$

The factor  $J$ , the mechanical equivalent of heat, is independent of the nature of the system in question. Its numerical value varies only with the system of units in which we measure the quantity of heat and external work. If we subject any system to any change we find in general the following changes in energy :—

- (1) A certain quantity of heat  $q$  is absorbed  $(+q)$  or evolved  $(-q)$ .
- (2) A certain external work  $+A$  is done by the system or  $-A$  done on the system.



- (3) Through these changes in heat or work a certain energy  $U$  is given out to the surroundings or to another system ( $+U$ ) or absorbed ( $-U$ ).

This change in the energy of the system must be equal to the difference between the work done and the heat absorbed.

$$U = A - q.*$$

If we allow a gas to expand from the volume  $v$  to  $v_1$ , keeping the temperature constant, the maximum work which can be performed is

$$A = RT \cdot \ln \frac{v_1}{v}.\dagger$$

In this isothermal expansion of the gas the total energy of the gas is not changed, therefore  $U = 0$ .

The energy necessary to perform the work is supplied by absorbing heat  $q$  from the surroundings so that

$$A = q.$$

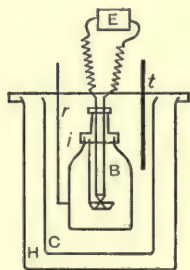
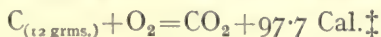


FIG. 1.

If we allow a system to evolve heat without performing work,  $A = 0$  and  $U = -q$ , i.e. the whole energy is obtained as heat. This case is realised practically in the determination of the calorific value of fuels in the Mahler-Berthelot calorimetric bomb. If we burn the ideal fuel, pure carbon, as pure wood charcoal in an excess of oxygen at high pressure the following reaction takes place completely :—



The whole decrease in energy of the system appears in this case in the form of heat, since in the closed vessel of the Mahler-Berthelot bomb external work cannot be done by the gases of

\* Obviously all the magnitudes in this equation must be expressed in the same energy units, e.g.  $A$  and  $q$  must both be in calories or both in mechanical units.

†  $\ln$  signifies natural logarithms (base  $e$ );  $\log$  signifies ordinary logarithms (base 10).

‡ The heat evolved is expressed in the so-called large calories (Cal.); a large calory is that quantity of heat which will heat 1 kilog. of water from  $0^\circ$  to  $1^\circ$  C. Its mechanical equivalent is 424 metre-kilograms.

combustion. The determination in the calorimetric bomb is performed in the following well-known way\* :—

About 1 grm. of coal is weighed off and burned in a thick-walled iron vessel B (Figure 1), enamelled inside, which is filled with oxygen at 10 to 25 atmospheres. The lid is tightened by a lead ring at *i*. The coal is pressed into a lozenge and a platinum wire is wound round it which is electrically heated by the battery E and ignites the coal. The outer vessel H is an insulator, *r* a stirrer, and *t* a thermometer divided into hundredths.

The heat of combustion is mainly transferred to the water surrounding the bomb in the copper vessel C and partly to the metal parts of the calorimeter. The latter amount, the water equivalent of the bomb, is previously ascertained by experiment. From the rise in temperature, the mass of the water, and the water equivalent the heat of combustion can be readily calculated as in the following example† :—

A calorimeter contains 2200 grms. of water. The water equivalent of the bomb and fittings (thermometer, stirrer, etc.) is 481 grms., i.e. the bomb and fittings are of such a weight that after multiplying it by their specific heat the number 481 is obtained, so that 481 grms. of water might be present instead of the bomb and fittings. 1 grm. of Montrambert coal was weighed off for the experiment. The rise in temperature was  $3.12^{\circ}$ , or  $3.15^{\circ}$ , after correcting for radiation losses. The heat evolved in combustion was, therefore,

$$(2200 + 481) \times 3.15 = 8.445 \text{ Cal.}^{\ddagger}$$

From this value must be deducted the amount of heat which is evolved by the combustion of the iron wire (used instead of the previously mentioned platinum wire for ignition) to iron oxide, and of the nitrogen, present in small quantities, to nitric acid (0.14 grms.).

Combustion of 0.025 grm. iron wire  $0.025 \times 1.6 = 0.040 \text{ Cal.}$

„ „ 0.14 grm.  $\text{HNO}_3$   $0.14 \times 0.23 = 0.032 \text{ Cal.}$

0.072 Cal.

\* Ost, *Lehrbuch der technischen Chemie*, p. 6 (Jänecke, Hanover, 1898).

† Von Juptner, *Die Bestimmung des Heizwertes von Brennstoffmaterialien*. Ahren's *Sammlung*, Bd. II, p. 401 (Enke, Stuttgart, 1898).

‡ Ost, *op. cit.*, p. 6.

The heat of combustion of 1 grm. of pure wood charcoal is 8.080, according to Favre and Silbermann, or more correctly 8.140 Cal., according to Berthelot and Bunte. It should be noted that the same quantity of heat which is liberated by the combustion of carbon to  $\text{CO}_2$  will be again absorbed when this compound is decomposed into its elements; this can be deduced at once from the first fundamental law.

If a fuel is allowed to burn under atmospheric pressure, as is always the case in heating, the theoretical heating value is clearly never attained, for two reasons. Firstly, the combustion under atmospheric pressure is incomplete, and there are also losses due to radiation and convection. Secondly, the gases produced perform external work against the pressure of the atmosphere; when using fuels this work is generally not utilised technically. Leaving out of consideration the heat losses due to the first reason given above, it is the same as if we were carrying out the combustion in the bomb at constant pressure instead of at constant volume. The amount of work performed by one mole (=molecular weight in grams) of a gas in being produced, that is to say, practically in expansion from volume 0 to the volume\* of one mole of a gas in the normal state, is

$$pv = RT,$$

where  $R$  is a constant, 1.99 Cal., and  $T$  the absolute temperature. Thus, if  $n$  moles of gas result from a combustion, or with a certain number of moles of gas already present, if  $n$  moles more result, we obtain a value for combustion at constant pressure which is  $nRT$  smaller than the heat of combustion at constant volume, the difference appearing as external work.

## 2. Hess's Law of Constant Heat-summation. Calculation of the Calorific Power of Fuels by Empirical Formulæ.

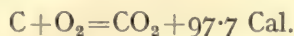
The law of constant heat-summation was put forward by Hess in 1840 before the discovery of the first fundamental law, that of the conservation of energy, though it is a natural consequence of this law. It states that the difference in energy between two

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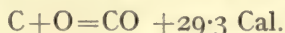
\* According to Avogadro's hypothesis, the same volume of two or more gases at the same temperature and pressure contains the same number of molecules, so that at the same temperature and pressure the same volume is occupied by one molecule of different gases.



given states of a system must be the same whatever path has been taken from one state to the other; for instance, in the direct combustion of carbon to carbon dioxide the following equation has been obtained :—



If the process is allowed to proceed in stages :—



in all 97.7 Cal.

Thus the calorific power of 1 kgrm. CO giving  $\text{CO}_2$  is  $68.4 \times \frac{1000}{28}$  Cal. The calorific power of 1 kgrm. H giving  $\text{H}_2\text{O}$  (steam) is 28800 Cal.

The water gas used technically for heating purposes consists ideally of equal volumes of carbon monoxide and hydrogen, i.e.  $\frac{1}{15}$  kgrm. H and  $\frac{1}{15}$  kgrm. CO. From the law of constant heat-summation the calorific power of such an ideal water gas can be accurately calculated as

$$\frac{1}{15} \cdot 28800 + \frac{1}{15} \cdot 2440 = 1920 + 2277 = 4197 \text{ Cal.}$$

Therefore the calorific power of fuels of given composition can be ascertained accurately from the calorific power of the single constituents, and thus the calorific power of natural coal can be calculated from the composition of the coal and the calorific power of its elements. The elements composing the coal can be determined by elementary analysis. However, they are present not as elements but as compounds, and for the exact calculation of the calorific power of the coal we require to know the heat of combustion of each of these separate compounds. For practical purposes the calorific power can be calculated within an error of  $\pm 3$  per cent by assuming that the carbon and sulphur are present as elements, but that all the oxygen of the coal is combined with the hydrogen as water. The hygroscopic water has also to be deducted. Thus we have as the formula for the calorific power

$$\frac{8140\text{C} - 28800(\text{H} - \frac{1}{8}\text{O}) + 2220\text{S} - 600\text{W}}{100},$$

when C, H, O, S, and W are expressed as units per cent.

### 3. Specific Heat of Gases. Pyrometric Heat Effect.

Let us assume that a system undergoes any change and that its temperature rises from  $T$  to  $T+t^\circ$ . This process can be carried out in two different ways:—

First way: We allow the process to take place at constant temperature  $T$ , when there is the change  $U_T$  in the energy of the system. We then warm the system, which has reacted and now possesses the specific heat  $c_1$ , by  $t^\circ$ . External heat  $c_1 t$  must be added for this purpose. The decrease in total energy is therefore  $U_T - c_1 t$ .

Second way: We warm the original system, of specific heat  $c$ , to the temperature  $T+t^\circ$ , thus adding heat  $ct$ .

We allow the system to react at this higher temperature, when a different decrease in energy  $U_{T+t}$  takes place.

In both cases we have attained the same final state in different ways,

$$\begin{aligned}\therefore U_T - c_1 t &= U_{T+t} - ct \\ \text{or } U_{T+t} &= U_T + t(c_1 - c).\end{aligned}$$

In general the magnitude  $U = A - q$  in chemical reactions is termed the heat of reaction  $Q$ . The heat of reaction is therefore the sum of the work done and the heat evolved, and thus

$$\begin{aligned}Q_{T+t} &= Q_T + t(c_1 - c) \\ \text{or } A_{T+t} &= Q_T + t(c_1 - c) + q_{T+t}.\end{aligned}$$

Thus this equation states that the heat of reaction changes with temperature in such a way that it increases as the temperature rises; it increases by the product of the rise in temperature and the difference between the specific heats of the disappearing ( $c$ ) and the resulting ( $c_1$ ) substances.

Before applying this equation to gas reactions we must briefly recall the fact that there is a difference between the specific heat of gases at constant pressure and constant volume. If we warm one mole of a gas at constant volume  $v^\circ$ , the heat added is equal to its specific heat  $c_v$ . But if the gas is allowed to expand at

the same time, i.e. if we determine the specific heat at constant pressure, work is done. When one mole of a gas is produced this work is equal to  $RT$  (p. 4).

When the temperature rises by  $1^\circ$  this work is

$$R(T+1) - RT = R.$$

Therefore the specific heat of the gas calculated on one mole at constant pressure  $c_p$  is

$$c_p = c_v + R.$$

We often require to know in practice in cases when high temperatures are attained not only the calorific power, but also the pyrometric heat effect, i.e. the maximum temperature which can be attained by combustion of the fuel in question. The maximum temperature which can be furnished by a fuel is obtained technically by dividing the calorific power by the sum of the products of the specific heat and the amount of the constituents of the gases of combustion. If 1 kgrm. of pure carbon is burnt by the amount of oxygen just necessary,  $3\frac{2}{3}$  kgrms. of  $\text{CO}_2$  are obtained with the evolution of 8140 Cal. Assuming the specific heat of  $\text{CO}_2$  at constant pressure to be 0.217 (according to Regnault, between  $10$  to  $210^\circ$ ), the maximum temperature which can be theoretically obtained is

$$t = \frac{8140}{3\frac{2}{3} \times 0.217} = 10230.$$

In combustion with the amount of atmospheric air just necessary, the theoretical maximum temperature is considerably smaller, since beyond  $3\frac{2}{3}$  kgrms.  $\text{CO}_2$  there are 8.82 kgrms. nitrogen to be heated by the 8140 Cal. furnished by the carbon ;

$$t = \frac{8140}{3\frac{2}{3} \times 0.217 + 8.82 \times 0.244} = 2790$$

(0.244 = specific heat of nitrogen).

When using excess of air the maximum temperature is naturally still lower. Moreover, this theoretically calculated temperature is never actually reached, for the following reasons :—

(1) Considerable heat is lost by radiation and conduction.

In practice this is to be avoided as far as possible.

- (2) At rather high temperatures decomposition takes place, and carbon dioxide dissociates into carbon monoxide to a certain extent dependent upon the temperature ; this absorbs a certain quantity of heat which is thus not available for raising the temperature.
- (3) At high temperatures the specific heat of gases increases above the values ascertained at lower temperatures and employed in the above calculation.

We will consider later the individual products of combustion. We may discuss somewhat more fully here the change in specific heat with temperature.

While the specific heats of oxygen, hydrogen, and nitrogen change comparatively little with temperature, the change in the specific heats of steam and carbon dioxide is comparatively rather large.

In what follows we shall always use the so-called mean specific heat, i.e.  $\frac{W}{T}$ , where  $W$  is the heat required to raise unit mass of the substance (taking one mole as unit) from absolute zero ( $-273^{\circ}$  C.) to the absolute temperature  $T$  ( $t^{\circ}$  C.  $+273^{\circ}$ ).

The change in the specific heat of gases with temperature can be usually expressed by the formula  $a+bT$ , where  $a$  and  $b$  are constants. According to Haber, the most probable values are those recalculated by Schreber\* from the extensive researches by Langen,† These are :—

For permanent gases . . . . .  $c_v = 4.879 + 0.00053t$ .

For steam . . . . .  $c_v = 7.456 + 0.001165t$ .

For carbon dioxide . . . . .  $c_v = 7.771 + 0.00189t$ .

By the aid of these data a correction can easily be introduced into the formula for the pyrometric heat effect, which, at all events, avoids the error caused through assuming the constancy of specific heat with temperature.

As to the specific heat at constant pressure, the remarkable fact has been discovered by Le Chatelier‡ that as a first approxi-

\* *Dingler's Polytechn. Journal*, 1903, **381**, 433.

† *Mitt. ii. Forschungsarbeiten a.d. Gebiete d. Ingenieurwesens*, Hf. 8, Berlin, 1903.

‡ *Compt. rend.*, 1887, **104**, 1780, and Haber. *Thermodynamics of Technical Gas Reactions*, p. 175.



mation the mean specific heat at constant pressure of the permanent gases is a constant.

For permanent gases . . . . .  $c_p = 6.8 + 0.00165T$ .

For steam (Haber) . . . . .  $c_p = 8.35 - 0.00165T$ .

For carbon dioxide . . . . .  $c_p = 6.8 + 0.0036T$ .

We shall use these figures later.

#### 4. The Second Fundamental Law. The Ideal Efficiency of Steam-engines.\*

Let us take one mole of an ideal gas in a cylinder, immersed in a large vessel of water (reservoir I) at temperature  $\dagger T$ , and compress it from volume  $v_1$  to the smaller volume  $v_2$ , when we shall have to perform the work

$$A = RT \ln \frac{v_1}{v_2} \dots (a);$$

a quantity of heat  $q = A$  will be given to the reservoir I, but owing to the size of the reservoir its temperature will not rise. We now introduce the gas, volume  $v_2$  and temperature  $T$ , into a second reservoir II, which is  $dT$  warmer. The cylinder and gas will absorb heat  $cdT$ , where  $c$  is the heat capacity of the cylinder and gas. During the heating the volume  $v_2$  is kept constant, and thus no external work is done. By allowing the gas to expand from volume  $v_2$  to  $v_1$  external work is now gained.

$$A + dA = R(T + dT) \ln \frac{v_1}{v_2} \dots (b).$$

A quantity of heat  $q + dq$ , equivalent to  $A + dA$ , is thus abstracted from reservoir II. Finally, we bring the gas, volume  $v_1$  and temperature  $T + dT$ , again into reservoir I and allow it to cool to the temperature  $T$ , keeping the volume  $v_1$  constant, i.e. without gaining work, when the quantity of heat  $cdT$  is evolved and all is as it was at first.

---

\* Cf. E. Meyer: "Die Bedeutung der Verbrennungskraft-maschine zur Erzeugung motorischen Kraft." Lecture to the Naturforscher-Versammlung at Breslau, 1904.

$\dagger$  The vessel is very large, so that small quantities of heat can be absorbed by the water without causing any appreciable rise in temperature.

Now, from equations (a) and (b) we have

$$dA = RdT \ln \frac{v_1}{v_2} \dots (c)$$

as the work which has been performed by the gas ; this is equal to the heat  $dq$  which has been transformed into external work during the transference of the amount of heat  $q + cdT$ , or neglecting  $cdT$  as of the second order compared with  $q$ , the quantity of heat  $q$ , from reservoir II to I. Dividing equation (c) by (a), we have

$$\frac{dA}{A} = \frac{dT}{T}$$

or since

$$A = q \text{ and } dA = dq,$$

we have

$$\frac{dq}{q} = \frac{dT}{T}$$

and also

$$\frac{dA}{q} = \frac{dT}{T}, \text{ i.e. } dA = q \frac{dT}{T};$$

in other words, the fraction  $q \cdot \frac{dT}{T}$  of the heat  $q$  transferred from reservoir II to I has been transformed into external work.

It should be noted that  $dA$  is hardly the work which can be yielded by raising the temperature of the system through  $dT$ . It is much more the increase in work which is obtained when the same process, which takes place in one direction at the temperature  $T$ , is reversed at the temperature  $T + dT$ .  $\frac{dA}{dT}$  is therefore the temperature coefficient of the capacity of the process in question to yield work. Combining the relationship

$$dA = q \cdot \frac{dT}{T}$$

with the first fundamental law of the mechanical theory of heat

$$U = A - q$$

we have

$$A - U = T \cdot \frac{dA}{dT}.$$

The latent heat of a chemical process is equal to the temperature coefficient of the maximum work multiplied by the absolute temperature.

An application of the second fundamental law best explains the mode of action of the steam-engine as well as of the more recently important turbine engine. The difference between steam-engines and steam-turbines is a constructional one; in the latter, which do not utilise the heat essentially better than the piston engine, the steam does not generate a reciprocating motion which then has to be transformed by indirect means into a rotary motion by using a crank mechanism, but acts directly on the rotating turbine wheel. Now, with the aid of the second fundamental law, we can show, on thermodynamical grounds, that both these types of engines have comparatively a very small heat efficiency. Taking two different temperatures  $T_1$  and  $T_2$  and calling the heat which goes in and out  $q_1$  and  $q_2$  we can adopt the form of the second law given on page 10,  $dq : q = dT : T$ , and write it  $\frac{q_1 - q_2}{q_1} = \frac{T_1 - T_2}{T_1}$ , where  $q_1 - q_2 = dq = dA$ .

The expression  $\frac{q_1 - q_2}{q_1}$  may be termed the economic coefficient; since the cyclical process described on page 9 is the most favourable which can be imagined, it follows that the economic coefficient can never be greater than  $\frac{T_1 - T_2}{T_1}$ .

Therefore, in these heat-engines the whole quantity of heat supplied by the fuel is never transformed into work, but part of it must always pass through the engine unchanged. It follows from the ratio

$$\frac{T_1 - T_2}{T_1}$$

that the fraction transformed into work is greater, the higher the difference in temperature.  $T_1$  is the temperature of the saturated steam as produced in the boiler, and at the greatest permissible boiler pressures it amounts to about  $200^\circ \text{C}$ . ( $473^\circ$  absolute);  $T_2$  is the temperature of the steam evolved from the engine and condenser, and is at least  $30^\circ$  ( $303^\circ$  absolute). Therefore, with absolutely ideal efficiency, in this case  $\frac{473 - 303}{473} = 0.36 = 36 \text{ per cent}$ , or about one-third of the available

heat is transformed into work. This theoretical efficiency can only occur when the whole available fall in temperature of the steam is

due to its expansion in the engine, causing the piston to reciprocate and yield work and thus change heat into work. But the heat is lost as work when the fall in temperature is due to transference of heat to cold bodies. This loss is obviously unavoidable in practical working, and it means that the economic coefficient is always lower than the ideal thermodynamic efficiency. There is a further loss in the utilisation of the calorific power of the fuel due to the fact that an indirect path is chosen by using steam. The gases of combustion produced by burning the coal in the boiler have a temperature of  $1200^{\circ}$  to  $1500^{\circ}$ . If the fall could take place from this high temperature, giving an expansion yielding work, we would have a considerably greater temperature difference at our disposal. By cooling to  $30^{\circ}$  the efficiency would then be

$$\frac{1473-303}{1473} \text{ to } \frac{1773-303}{1773},$$

i.e. 72.8 to 82.9 per cent.

Together with part of the temperature difference a large part of the calorific power of the steam is destroyed through transferring the heat of the gases of combustion by conduction to the steam at  $200^{\circ}$ , and thus causing the fall in temperature giving the working expansion to begin at  $200^{\circ}$  instead of at  $1200^{\circ}$  to  $1500^{\circ}$ . The best steam-engines transform into useful work only 10 to 13 or as a maximum 15 per cent of the heat evolved by the combustion of the coal in the boiler.

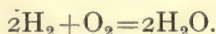
On account of the allowable boiler pressures, and for other reasons, an essentially higher temperature difference cannot be attained when using steam, which therefore appears thermodynamically disadvantageous as an intermediary in the transformation of heat into work, however convenient it may be from a technical standpoint. Considering what has been said above it appears most economical to allow the fall of temperature to begin right from the high temperatures of the gases of combustion, when therefore the gases of combustion themselves will expand in the motor cylinder and yield work. This requirement is realised in combustion engines, in which combustion and evolution of heat take place in the motor cylinder itself. Since only gaseous fuels can come into consideration here, these are also called gas-engines or gas-motors.



We will see shortly that thermodynamically these appear much more promising than steam-engines.

**5. The Maximum Work of a Chemical Process and the Deduction of the Law of Mass Action in a General Form.**

To answer the question how much external work can be furnished by a chemical reaction such as the combustion of a gaseous fuel, as in working a gas-motor, we have to consider quite generally the question of the maximum work of a chemical process. We will do this for a particular example, the formation of water from its elements.



Let us take a space filled with hydrogen at the concentration  $C_{\text{H}}$  and oxygen at the concentration  $C_{\text{O}}$ . We will now introduce molar quantities of both gases into a second space in which they possess the smaller concentration  $c_{\text{H}}$  and  $c_{\text{O}}$ . We thus obtain an amount of work (p. 9)

$$2RT \cdot \ln \frac{C_{\text{H}}}{c_{\text{H}}} + RT \cdot \ln \frac{C_{\text{O}}}{c_{\text{O}}}$$

Formation of water takes place in the second space yielding water vapour at the concentration  $c_{\text{W}}$ . We will bring this water vapour isothermally and reversibly into the first space at the higher concentration  $C_{\text{W}}$ . This requires an amount of work

$$2RT \cdot \ln \frac{C_{\text{W}}}{c_{\text{W}}}.$$

The work gained in the whole process is therefore

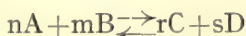
$$A = 2RT \cdot \ln \frac{C_{\text{H}}}{c_{\text{H}}} + RT \cdot \ln \frac{C_{\text{O}}}{c_{\text{O}}} - 2RT \cdot \ln \frac{C_{\text{W}}}{c_{\text{W}}}$$

or

$$A = RT \cdot \ln \frac{C_{\text{H}}^2 \cdot C_{\text{O}}}{C_{\text{W}}^2} + RT \cdot \ln \frac{c_{\text{W}}^2}{c_{\text{H}}^2 \cdot c_{\text{O}}}.$$

Now the maximum work  $A$  must be independent of the nature of the reaction mixture in space II, which, indeed, only plays the part of an intermediate body undergoing no apparent change during the reaction. But this is only possible if at constant temperature the expression  $RT \ln \frac{c^2 W}{c^2 H \cdot c_O}$ , and therefore  $\frac{c^2 W}{c^2 H \cdot c_O}$ , is constant.

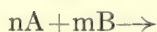
This expression is nothing else than the law of mass action of Guldberg and Waage. Quite generally, if  $n$  moles of the substance  $A$  react with  $m$  moles of the substance  $B$ , giving  $r$  moles of the substance  $C$  and  $s$  moles of the substance  $D$ , i.e. if the reaction



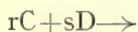
takes place, then in the state of equilibrium we will have

$$K = \frac{C^r_C \cdot C^s_D}{C^n_A \cdot C^m_B}.$$

We could carry out this process for any other reaction and in the same way arrive at the law of mass action in its most general form. Since  $K$  numerically expresses the state of equilibrium of the reacting substances, we can attain the same equilibrium whether we allow the reaction to proceed from left to right,



or from right to left,



In both cases we must attain the same final state, namely, the state of equilibrium.

If the system in question is left to itself in the state of equilibrium this state will be maintained for an infinite time. However, kinetically considered, equilibrium should not be regarded as a state of complete absence of reaction. We must rather assume that the state of equilibrium is due to the fact that the velocities of both reactions leading to equilibrium have become equal, so that as many molecules of the substances on the right-

hand side decompose per unit of time as are formed from the left-hand side. This view leads to another deduction of the law of mass action which is not so strict, since it is kinetic, but on this account is more obvious. Kinetically, then, two or more molecules will react when they collide in such a way as to disrupt the atomic linking of the molecules. The reaction-velocity will accordingly be proportional to the number of these collisions, which again is proportional to the number of molecules in the unit of concentration of the reacting substances. Therefore, we have for the velocity of change  $v_1$  from left to right,

$$v_1 = k_1 \cdot C_A^n \cdot C_B^m.$$

The reaction-velocity  $v_2$  from right to left is

$$v_2 = k_2 \cdot C_C^r \cdot C_D^s.$$

$k_1$  and  $k_2$  are constants, the velocity coefficients of the two reactions leading to equilibrium. In the state of equilibrium, when both velocities are equal,  $v_1$  equals  $v_2$ , i.e.

$$k_1 \cdot C_A^n \cdot C_B^m = k_2 \cdot C_C^r \cdot C_D^s \text{ or } \frac{C_C^r \cdot C_D^s}{C_A^n \cdot C_B^m} = \frac{k_1}{k_2}.$$

The quotient  $\frac{k_1}{k_2}$  is naturally a constant, which is the equilibrium-constant  $K$ . For gases the partial pressure  $P$  of each of the components can be introduced into the equilibrium-constant instead of the concentration  $C$ , giving

$$K = \frac{P_C^r \cdot P_D^s}{P_A^n \cdot P_B^m}.$$

In a subsequent chapter we will consider more fully the application of the law of mass action, and we will use the above expression for the maximum work of a chemical process. Taking the initial concentrations  $C_H$ ,  $C_O$ , and  $C_W$  equal to 1 in the

equation for A given above, we find that the maximum work is

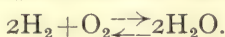
$$A = RT \cdot \ln \frac{c_W^2}{c_H^2 \cdot c_O} = RT \cdot \ln K.$$

Thus from the equilibrium-constant of a chemical reaction we can calculate the maximum work of that reaction at a given temperature T.

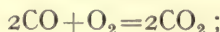
Hence in principle we have now answered our question as to the working effect of the gaseous fuel in gas-motors.

However, there is frequently some difficulty in determining K.

To ascertain the working capacity of the combustion of hydrogen we must find the equilibrium of the reaction



Read from right to left this is the equation of the dissociation of steam, which we must first ascertain. The combustion of carbon monoxide is a second practical case,



the waste gases from blast furnaces are rich in carbon monoxide, and can be advantageously employed for driving gas-engines. To determine the maximum work of this process we must solve the problem of determining the dissociation of carbon dioxide.

According to Nernst and Wartenberg,\* the degree of dissociation  $\alpha$ , i.e. the number of moles per cent dissociated, is at room temperature ( $T=290^\circ$  abs.):—

$$\text{Water} \dots\dots\dots \alpha = 0.537 \times 10^{-25}.$$

$$\text{Carbon dioxide} \dots\dots \alpha = 1.10 \times 10^{-31}.$$

According to Nernst,† when  $H_2$  or CO at 1 atmo., and the oxygen of the air at 0.2 atmo. partial pressure, are burnt to  $H_2O$  or  $CO_2$  at 133 atmo., we have

$$A = RT \cdot \ln \frac{100^3 \times 2 \times 0.2}{\alpha^2 \times 0.133^2}.$$

For ordinary logarithms  $R=4.571$ ; thus

for  $2H_2O$ ,  $A=108000$ , the heat of combustion  $q=115000$ ,

for  $2CO_2$ ,  $A=133000$  „ „ „  $q=136000$ .

\* Gött. Nachr., math.-naturwiss. Kl., 1900, Heft I.

† Physikalisch-Chemische Betrachtungen ü. d. Verbrennungsprozess in Gas-motoren, pub. Springer, Berlin, 1905.



Under the above conditions  $A$  is not very different from the heat of combustion. On this account, in many cases at a given temperature  $A$  is simply taken as equal to the heat of combustion, which is naturally a rough approximation, since  $A$  can be larger or smaller than  $q$ .

We may now consider the working of the gas-engine.

### 6. Gas-engines.\*

It is well known that these engines, also called explosion motors, yield considerably less work than would answer to the ideal efficiency calculated on the above basis.

One reason for this is the very considerable loss resulting from radiation, especially at higher temperatures, and convection at lower temperatures. Further, in practice, during expansion the gas mixture cannot be brought to room temperature adiabatically, i.e. without loss of heat. Nernst gives the following theoretical solution of the problem of constructing the gas motor to furnish the theoretically calculated maximum efficiency. Hydrogen (or CO) and oxygen are compressed adiabatically (i.e. without losing heat to the surroundings) at such a high temperature that after mixing the gases the dissociation remains almost complete and formation of water does not occur to any appreciable extent. Thus on an adiabatic expansion, owing to the heat developed by gradual formation of water, more work is obtained than was performed during compression, and this increase is the maximum work. The impossibility of carrying this out in practice is obvious, though the attempts to increase the compression in the four-stroke motor, and forms of construction such as the Diesel engine, point to a distinct tendency to approximate to this ideal case. To render this clear we will briefly describe the practical operation of these two types of gas-engines.

In the four-stroke motor a cast-iron cylinder is closed in front by a piston, whose reciprocating motion is transformed into rotary motion by crank mechanism. On the crank shaft there is a fly-wheel which, owing to its large mass, maintains the movement of the engine when the driving force is not acting. At the back end of the cylinder there is a space, the combustion space, which is left free by the piston even in its innermost

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\* Cf. E. Meyer, *loc. cit.*

position. It has two openings (shown in Figure 2), which are closed by valves and can be opened at the right moment by the regulation of the engine. The gases of combustion are passed into the atmosphere through the exhaust valve *a*, after performing work, while the explosion mixture of air and gas enters the cylinder through the inlet valve *b*. There is a mixing valve *c* in the pipe leading to the inlet valve at the point where the gas pipe leads into the air pipe. While the piston goes outward for the first time, the inlet valve *b* and the mixing valve *c* are open and the explosive mixture of air and gas, i.e. the charge, is thus sucked into the cylinder (suction stroke). When the piston goes

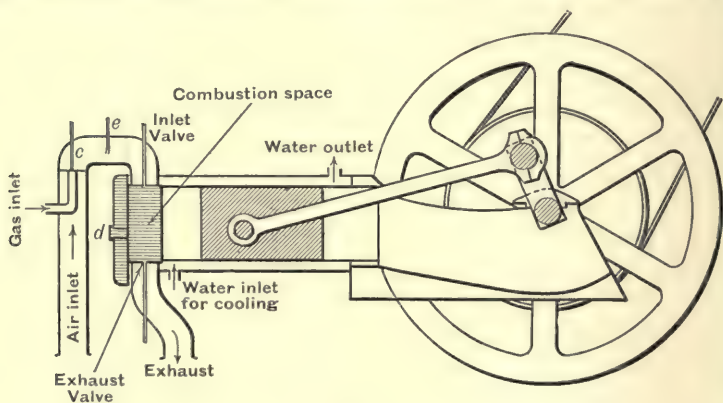


FIG. 2.

backward and the valves *b* and *c* are closed the space behind the piston containing the charge is continually lessened and the pressure increases. The charge is thus compressed into the combustion space (compression stroke). When the piston has again reached its innermost position, an electric spark is made at the point *d* in the combustion space, which explodes the charge and causes it to expand. Its temperature and pressure rise very greatly almost instantaneously and the piston moves outward. In consequence of the increase in volume, the temperature and pressure of the gases of combustion steadily fall; this fall in temperature is due to the expansion which is yielding work, since part of the heat of the gases of combustion is transformed into work (working stroke). When the piston has reached its outermost position for the second time the exhaust valve *a* opens, the gases of combustion escape into the atmosphere, and as the piston

goes back are completely removed except for the quantity remaining in the combustion space (exhaust stroke). The working cycle can now begin again with a new suction of a fresh charge. This working cycle thus consists of two forward and two backward movements or of four strokes, and is therefore called the four-stroke cycle.

Since only one of the four was a working stroke the cycle could not be performed without the help of the fly-wheel, which maintains the movement of the engine during three of the strokes. More recently the so-called two-stroke cycle has become prominent, in which the inflow of the charge and the outflow of the exhaust is effected by the aid of a special charging pump. In this case only the combustion stroke and the working stroke take place in the motor cylinder itself. However, thermodynamically this is not a fundamental change from the four-stroke cycle. The four-stroke and, with suitable changes, the two-stroke motor can be best explained graphically by representing the positions of the piston at any moment as abscissæ and the corresponding gas pressures as ordinates.

The diagram (Figure 3) is an indicator diagram obtained by

E. Meyer for the 10-h.p. illuminating gas-engine at the Institute for Technical Physics at Göttingen, in which the temperatures and gas pressures have been inserted at the more important points. It can be seen from the diagram that in this engine the temperature at the end of

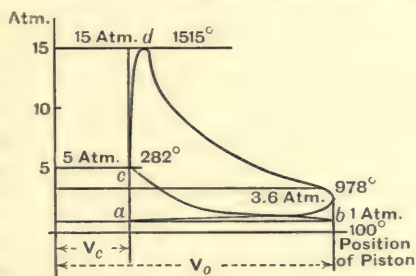


FIG. 3.

the explosion, i.e. the temperature of combustion, was  $1515^{\circ}$  C., and the temperature at the end of the working expansion was  $978^{\circ}$  C. The degree of compression is very important in these motors, i.e. the ratio of the total volume of the gas charge  $V_0$  at the end of the suction to the volume of the combustion space  $V_c$ , since the higher the compression of the

charge is made before explosion the more the combustion gases can expand again and thus the greater are the temperature differences available for the gas-engine. In the Göttingen engine the



degree of compression was 3.8. The most important means of obtaining the best possible heat efficiency in the gas-engine (in the four- and two-stroke motors) is the highest possible degree of compression. Practical considerations with reference to the strength of the engine and the friction at the piston and bearings stand in the way of this theoretical requirement, and 35 to 40 atmospheres at most is the maximum pressure allowable. While, therefore, in the ideal limiting case described by Nernst practically the whole free energy would be obtained in the form of maximum work, in the practical working of the gas motor the efficiency is determined by the working fall in temperature.

The thermodynamic heat efficiency of the Göttingen engine with a degree of compression of 3.8 was approximately 33 per cent, while a 70-h.p. gas-engine with a degree of compression of 8.0 showed an approximate thermodynamic efficiency of 44 per cent. Yet these values are only ideal cases which cannot be attained practically, since numerous losses of heat take place.

Thus on the one hand losses occur owing to incomplete combustion (4 per cent of the ideal value in the Göttingen engine, 2.3 per cent in the 70-h.p. engine); useful heat is consumed by the suction and exhaust (4.2 per cent and 5.2 per cent), and there is also a loss by mechanical friction (16.4 and 7.8 per cent). At the high temperatures reached in the cylinder it would be impossible to drive the engine without surrounding the walls of the cylinder and the combustion space with cooling water. Heat is here lost to the water, and in the above-mentioned engines this loss amounted to 15 per cent and 14.9 per cent of the ideal value. If an actual heat balance is now drawn up we see that only 60.2 per cent of the available work was actually obtained in the Göttingen engine, and 68.2 per cent in the 70-h.p. engine. Therefore, in these two engines only 19.9 and 30.3 per cent of the ideal efficiency was attained instead of 33 to 44 per cent. On account of the danger of explosion (see next section, 7) in benzine and petroleum motors it is difficult to operate, in the manner described, above a degree of compression of 4, since very easily inflammable compounds are present in the benzine and petroleum. Only an efficiency up to 22 per cent can be obtained with these engines, according to E. Meyer. Since, therefore, in the gas-engines we have mentioned an efficiency of 19.9 to 30.3 per cent can be



attained we see that thermodynamically they excel the best steam-engines, which have an efficiency of 15 per cent. But in practical use we are not only concerned with the efficiency itself, but also with the cost of fuel. While motors fed with illuminating gas, benzine, and petroleum prove profitable on a small scale, it would be too expensive to drive large engines with these fuels, so that in spite of their thermodynamic superiority they cannot displace steam-engines. In order to utilise this thermodynamic superiority economically a gas is used for gas-engines which gives heat almost as cheaply as coal does. This requirement leads us to the employment of power gas, producer gas, practically pure carbon monoxide, or of water gas, a mixture of carbon monoxide and hydrogen; both these kinds of gas can be used to feed gas-engines and we will consider them later. In the valuable lecture mentioned above, E. Meyer shows that 80 per cent of the heat of combustion of the coal used to make the producer gas was recovered as the heat of combustion of that gas. If the gas-engine has an efficiency of 31.6 per cent, as in the installation examined by Meyer, 25.3 per cent of the actual heat in the coal will be transformed into useful work in the motor. The gas motor will be of special value in cases where combustible gases are obtained to a certain extent as by-products, as in iron-smelting (page 116).

As well as producer gas, obtained from so-called producers, i.e. furnaces directly constructed to yield these gases, the waste gases evolved from blast furnaces (see cap. IV) are also rich in carbon monoxide. While half this waste gas must be used for the preliminary heating of the blast, the other half has still to be disposed of. It used to be burnt under boilers, but this means an uneconomical utilisation of the combustible gas, since a blast furnace with a daily production of 200 tons can produce at most 2500 h.p. with the available waste gases, using steam-engines. In this case, where a gaseous fuel is directly available, the gas-engine is undoubtedly preferable, and, in fact, the same quantity of waste gas will produce at least 5000 to 6000 h.p., i.e. fully 3000 h.p. more than the steam-engine produces under the same conditions. Apart from the difficulty generally experienced in the gas-engine industry in the production of suitable gaseous or liquid fuel, which is not always cheap and easy, we can come to the conclusion that the thermodynamic superiority of the gas

motor has also become economic. Comparing heat efficiency in the best examples of steam-engines on the one hand and gas-engines on the other hand, the numbers are 15 per cent (see page 12) against 25 per cent, referred to coal.

### 7. Gas Explosions \* and Solid Explosives.†

In considering gas motors we met with mixtures which can react on ignition, giving a corresponding quantity of energy which appears in the form of external work. This combustion of the gaseous mixture can take place explosively under certain conditions. It is of interest to follow the further course of the combustion of explosive gases and to study the nature of the velocity of propagation of gas explosions. If an explosive gas mixture in a long tube is ignited at one end, the explosion is propagated at first with a moderate velocity; but for the mixture of a gaseous fuel with oxygen, for example, this velocity steadily rises, and after a certain distance, either metres or centimetres according to the nature of the mixture, it attains a definite maximum velocity which is characteristic for the gas mixture in question. This velocity amounts to 2820 met. per sec. for hydrogen, 2300 for methane, and 2450 for acetylene, the gases in each case being mixed with an equivalent quantity of oxygen. The ignition itself is effected by locally heating the explosive gas; there is a lower limit for the amount of heat just necessary for ignition. The local evolution of heat owing to chemical change must be just greater than the fall in temperature owing to the heat spreading from a point, to cause self-heating and thereby to bring about a sufficient reaction for the next layer to be ignited. In explosion it is therefore necessary first to obtain a definite just sufficient minimum temperature locally, the height of which essentially depends on the reaction-velocity, and is characteristic for each gas mixture; this is called the temperature of inflammation. According to Le Chatelier and Mallard,‡ propagation of combustion after ignition can occur in two essentially different ways. It may take place

\* Nernst, *Physikalisch-chemische Betrachtungen über den Verbrennungsprozess in Gasmotoren*, pub. Springer, Berlin, 1905.

† E. Baur, *Themen d. physikalischen Chemie*, Leipzig, Akad. Verlagsge. m.b.H., 1910, p. 12 et seq.

‡ *Rech. expériment. et théor., etc., Ann. des Min.*, Sept.-Dec., 1883.

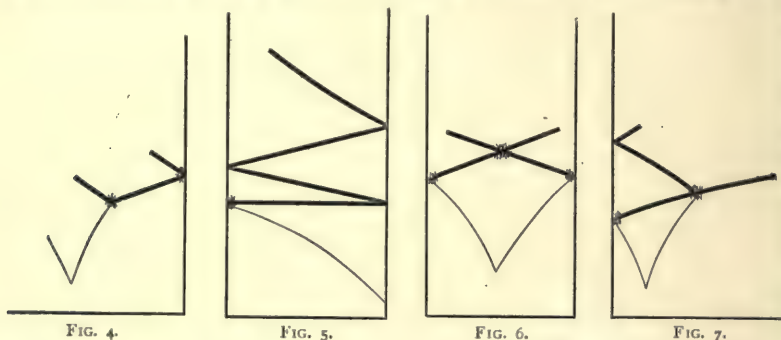
by "slow combustion," when the high temperature of the layer first inflamed by ignition is spread by conduction of heat, thus bringing the neighbouring layers to the temperature of inflammation. It may also take place through an "explosive wave," in which case the temperature rises owing to the increase of pressure caused by the reaction taking place almost wholly adiabatically (i.e. without giving heat to the surroundings) in consequence of the high reaction-velocity. Moreover, the concentration of the reacting gases is increased by this rise in pressure, and as we shall see later (II, 1), this brings about a higher reaction-velocity. A very powerful compression wave generated in a gas mixture can both start combustion (see page 24; early ignition in gas mixtures) and also propagate it; it passes through gas mixtures with considerably greater velocity than an ordinary compression wave, since in the compressed unburnt layer, owing to the inflammation, there is a very strong development of pressure, which, according to the principles of the theory of waves, must raise the velocity of propagation. The velocity of explosive waves is markedly greater than the velocity of sound (about  $1\frac{1}{2}$  to 2 times). We may draw the following picture of what takes place in an explosive gas mixture after ignition. First we have the state of slow combustion. Heat is transferred to the neighbouring layers by conduction, and the velocity of propagation is only a few metres per sec. But since combustion is connected with increase in pressure the adjacent unburnt layers are continually compressed. This increases both the reaction-velocity and the velocity of inflammation. When the compression in the unburnt layers has reached such a height, i.e. when such an increase in temperature has been effected, that self-ignition takes place, the strong compression wave now produced must propagate itself with simultaneous inflammation at a very high velocity, i.e. we have spontaneous development of Berthelot's "explosive wave." An ingenious photographic method for observing explosive waves has been worked out by Dixon.\* A horizontal glass explosion tube with an electric ignition device is placed in front of a camera containing a rotating roller covered with a photographic film. The explosion flame appears on the film as an inclined line of light, and from its angle to the horizontal, at a known velocity of the film, the velocity of explosion

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\* *Phil. Trans.*, 1903, 200, 315-352.



can be ascertained. Diagrams of Dixon's photographs (Nernst) are shown in Figures 4 to 7. The thin lines representing a weaker light show the path of the inflammation wave, while the thicker lines representing a stronger light show the path of the explosive wave. It will be seen that the inflammation wave first starts slowly, goes faster, and finally turns into the explosive wave. At the transition point a backward wave of compression, the so-called retonation wave, is sent backwards in the already partially burnt gas and is then thrown back from the walls of the explosion tube so that it goes forwards and backwards through the tube several times. As a rule a slow combustion striking the walls gives rise to an explosive wave, a phenomenon which is fundamental from a practical point of view. The crossing of a



compression and a slow combustion wave releases an explosive wave owing to the instantaneous high compression which results (see specially Figure 6). It is notorious in gas motors and in the so-called explosion motors that the occurrence of explosive waves is very bad for the motor. The motor itself is disturbed too much, owing to the violent shaking by the explosion, and its working thus suffers, and again the considerable movement in the gas, due to the formation of the explosive wave, prejudices the working power of the explosion of the ignited gas mixture. It is therefore necessary to take care in constructing motors that the gas is completely burnt in the motor before it can form the explosive wave, and for this purpose the positions of the points of ignition and the dimensions of the explosive cylinder must be dimensioned. Nernst suggests that Dixon's experiments show it to be most probable that an ignition right on the piston wall, and as far as possible distributed between several points, would



most readily protect this very sensitive part of the surroundings of the explosion space from the action of the explosive wave, since it should be possible to limit the formation of explosive waves by a suitable distribution of the various points of ignition. Very similar phenomena are observed in

### Solid Explosives.\*

These are substances which decompose spontaneously, evolving heat and gaseous reaction-products. When such explosives, e.g. gunpowder, are ignited in the open, inflammation occurs instead of explosion; this answers completely to the inflammation of gases; in both cases heat waves are produced. But when solid explosives are ignited in a closed vessel, an adiabatic compression takes place in the same way as with gases, which heats the gaseous products of reaction forming the pressure wave, the so-called explosive wave. Its action, however, is actually about 1000 times greater, corresponding to the fact that the velocity of sound is much higher in solid bodies than in gases, so that once it has been induced the explosive wave moves much more rapidly than in gases. There are three characteristic factors of explosives: the explosion pressure, the sensitiveness, and the shattering power. The following table gives the explosion pressure of different explosives, according to Nobel and Abel, at three different densities of charge  $\Delta$ , i.e. grms. of explosive per c.c. explosion space:—

| $\Delta$ | Gunpowder. | Nitro-glycerine. | Guncotton. | Picric Acid. | Ammonium Nitrate. | Mercury Fulminate. |
|----------|------------|------------------|------------|--------------|-------------------|--------------------|
| 0.4      | 1,587      | 5,640            | 5,912      | 5,523        | 3,211             | 2,072              |
| 0.5      | 2,112      | 7,829            | 8,502      | 7,982        | 4,779             | 2,686              |
| 0.9      | 5,126      | 25,270           | 38,500     | 38,310       | 36,250            | 5,683              |

In the case of the explosion of solid explosives, as in that of gases, transitory and local higher pressures must result as soon as the wave motion is brought about through any inequality. The pressure values given in the above table only represent—apart from conduction of heat—the permanent final pressure of the explosion. The final pressures produced by small charge densities drive projectiles from gun-barrels or cannon bores†

\* E. Baur, *loc. cit.*

† At high densities of charge (for granite, torpedoes, mines) the higher pressures mentioned above occur locally and instantaneously, thus causing the enormous explosive action of these projectiles.

just as explosion motors are driven by the explosion of gas mixtures. The work performed by the explosive is simply that of an adiabatic expansion as in the gas-engine. This adiabatic work for one molecule of gas is

$$\text{Const.} \int_{v_1}^{v_2} \frac{dV}{V^K} = \frac{R}{K-1} (T_1 - T_2),$$

where  $v_1$  and  $v_2$  are volumes per mole before and after explosion,  $K = \frac{C_P}{C_V}$  the ratio of the molecular heats (specific heat

per mole) at constant pressure and constant volume,  $T_1$  and  $T_2$  absolute temperatures before and after explosion.

The stability of an explosive may be measured by the detonating temperature, i.e. the minimum temperature which is just sufficient to cause inflammation. The heat necessary for this purpose can also be produced mechanically by the blow of a hammer, and by concussion in a rifle. The sensitiveness of an explosive can be measured by determining the height through which a 2-kgm. hammer must fall to explode the explosive by furnishing the necessary heat. The following table shows the connection between the strength of the blow and the temperature of detonation.

| Explosive.             | Composition.   | Detonating Temperature. | Sensitiveness. Centimetres distance through which the 2 kgm weight falls. Hammer surface = 0.385 sq. cm. |
|------------------------|--|-------------------------|--|
| Mercury fulminate . .  | $\text{Hg}(\text{CNO})_2$  | 160                     | 2  |
| Dynamite . . . .       | { 75% Trinitroglycerine<br>25% Kieselguhr }  | 180                     | 7  |
| Blasting gelatine . .  | { 93% Trinitroglycerine<br>7% Collodion cotton }                                       | 180                     | 12   |
| Collodion cotton . . . | { Nitrocellulose, with<br>12% Nitrogen }   | 190                     | 100  |
| Picric acid . . . .    | $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$                                       | >225                    | 95   |
| "Ammonium-carbonite" . | { 82% $\text{NH}_4\text{NO}_3$<br>10% $\text{KNO}_3$<br>4% Nitroglycerine<br>4% Meal } | >225                    | 110  |

We see that mercury fulminate takes the first place as far as sensitiveness is concerned. The last place in the list is filled by a safety explosive, which owes its name to the fact that the heat generated by the explosion is not sufficient to "initiate" its own explosion, so that such safety explosives are very important for coal-mining. While the temperatures of inflammation of solid explosives lie roughly at about  $200^{\circ}$ , the analogous temperatures for gases are about  $500^{\circ}$  to  $600^{\circ}$ , therefore solid explosives "go off" much more readily, which is a point of the utmost importance for the development of explosive waves in solid bodies. The possible heat of compression of solid bodies is much smaller than in the case of gases and only suffices to cause an adiabatic heat of  $200^{\circ}$  to  $300^{\circ}$  at most. If such rises in temperature were insufficient for ignition the slow inflammation already mentioned would never have the opportunity of turning into rapid explosion. We have mentioned that the velocities of explosive waves are essentially greater in solid explosives than in gases, and special chronographic methods have been developed for their measurement. This velocity is intimately connected with a characteristic factor of explosives, the shattering power.

### 8. Change of the Free Energy Gradient with Temperature.

In the equation  $A = RT \cdot \ln K$

$A$  represents that part of the change of energy associated with the reaction which can be absolutely obtained as external work and therefore as heat, which is thus "free." Hence it is called the free energy. We may speak of the free energy of formation of a compound, and of the free energy gradient of a reaction, in each case meaning  $A$ .  $A$  is also called the affinity of the reaction.

In its simple form the expression  $A = RT \cdot \ln K$  only holds for a quite definite temperature, as we have mentioned on page 16. To consider the influence of temperature, we combine the first two fundamental equations

$$U = A - q$$

$$q = T \cdot \frac{dA}{dT},$$

and obtain, by eliminating  $q$ ,

$$A - U = T \cdot \frac{dA}{dT}.$$

Instead of  $U = A - q$ , let us insert the heat of reaction  $Q$ , which is the heat evolved at temperature  $T$  when the reaction takes place without performing external work,

$$A - Q = T \cdot \frac{dA}{dT} \quad (1).$$

Since  $A = RT \cdot \ln K$ , we obtain by differentiation

$$dA = R \cdot \ln K dT + RT \cdot d \ln K.$$

Substituting in (1),

$$RT \ln K - Q = RT \ln K + RT^2 \cdot \frac{d \ln K}{dT},$$

$$\therefore Q = -RT^2 \cdot \frac{d \ln K}{dT} \text{ or } \frac{d \ln K}{dT} = -\frac{Q}{RT^2}.$$

This formula means that when a chemical system is heated at constant volume, the equilibrium shifts to the side towards which the reaction proceeds with the absorption of heat. By combining the first and second fundamental equations we find that at absolute zero,  $T = 0$ ,

$$A_0 = U_0 \text{ and therefore } = Q_0,$$

i.e. at absolute zero the change in free energy is equal to the decrease in total energy and equal to the heat of reaction \*  $Q_0$

which (since the reaction proceeds without performing external work) is equal to the heat of combustion at absolute zero.

The heat of reaction  $Q_T$  at temperature  $T$  is obtained from  $Q_0$  and the difference in specific heat between the reacting substances and the reaction-products (p. 6)  $c_r - c_p$ ,

$$Q_T = Q_0 + T(c_r - c_p).$$

The specific heat may be expressed (p. 8),

$$c = a + bT;$$

so for the reacting substances,

$$c_r = a_r + b_r T,$$

---

\* Heat of reaction = "Wärmetönung," which has often been "translated" as "heat-toning." —  $Tr$ .



and for the reaction-products

$$c_p = a_p + b_p T,$$

$$\therefore c_r - c_p = a_r - a_p + (b_r - b_p)T.$$

For simplicity calling  $a_r - a_p = a$ ,  $b_r - b_p = \beta$ , then

$$Q_T = Q_0 + aT + \beta T^2.$$

For a given temperature  $T$  we have

$$d \ln K = -Q_T \cdot \frac{dT}{RT^2},$$

and substituting the above value for  $Q_T$ ,

$$d \ln K = -\frac{Q_0}{RT^2} dT - a \frac{dT}{RT} - \beta \frac{dT}{R}.$$

Integrating,

$$\ln K = \frac{Q_0}{RT} - \frac{a}{R} \ln T - \frac{\beta}{R} T + \text{const.}$$

Multiplying by  $RT$ , and substituting  $A_T$  for  $RT \cdot \ln K$ ,

$$A_T = Q_0 - aT \ln T - \beta T^2 + R \cdot \text{const. } T.$$

This formula holds when all the reacting gases and the gases produced are at 1 atmo. pressure. Quite generally, if  $n$  moles of the reacting gases A and B are at pressure  $p_A$  and  $m$  moles at pressure  $p_B$ , the energy furnished by the reaction will be increased by the work corresponding to the expansion of  $n$  moles of A and  $m$  moles of B, i.e. by

$$nRT \cdot \ln p_A + mRT \cdot \ln p_B.$$

The  $r$  and  $s$  moles of gases C and D produced at the pressure  $p_C, p_D$  will require for compression to 1 atmo.

$$r \cdot RT \cdot \ln p_C + s \cdot RT \cdot \ln p_D.$$

So that in its general form the equation of the free energy gradient will be

$$A_T = Q_0 - aT \ln T - \beta T^2 + BT + RT \cdot \ln \frac{p_A p_B}{p_C p_D},$$

using a new constant  $B$  instead of  $R \times \text{const.}$  Introducing the absolute value 1.99 of the gas-constant  $R$ , and the factor 2.3 for conversion of natural logarithms into ordinary logarithms, we have

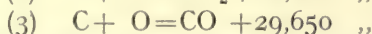
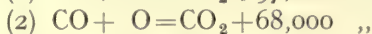
$$A_T = Q_0 - a \times 2.3 T. \log. T - \beta T^2 + BT + 4.58 \log. \frac{P_A P_B}{P_C P_D}.$$

Knowing the equilibrium-constant or the free energy gradient at a given temperature, we can find the only unknown,  $B$ , remembering that at equilibrium the free energy gradient  $A_T = 0$ .

We will now apply this general formula for the free energy gradient to some reactions of practical importance and thus explain its significance more fully.

### 9. Application to some Technically Important Processes of Oxidation and Reduction. Producer Gas, Water Gas, Reduction of Metals and Deacon Process.\*

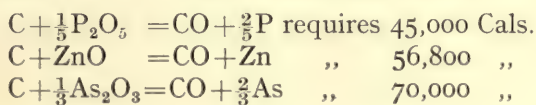
In technical reduction-processes there are three main reactions which have usually to be studied :—



The first of these seems best from an economic point of view, since twice as much oxygen can be removed from other substances with the same quantity of carbon as in other reactions and at the same time most heat is produced. However, in spite of the high heat of the combustion of reaction (1), carbon itself only reduces the most easily reducible compounds, such as the oxides of silver, copper, and lead. The great technical example is the reduction of sodium sulphate by carbon in the Leblanc process. As we shall see, it is mainly reaction (2), and only to a small extent reaction (3), which is important in the metallurgy of iron. Reaction (3) comes more to the front when the compound is harder to reduce. In the blast furnace it brings about the reduction of oxides which are harder to reduce than iron, of silicic and phosphoric acids, and of manganic oxide. We must thus assume that the energy of these three reducing reactions follows the reverse order to the heats of reaction.

\* Cf. Bodländer, *Z. f. Elektrochem.*, 1902, 8, 833. Jüptner, *Z. f. anorg. Chem.*, 39, 40 and 41. Haber, *Thermodynamics of Technical Gas Reactions*.

It follows from the heats of reaction that reduction by reaction (2) yields more energy than by reaction (1). The combination with one atom of oxygen, which we must always keep before our mind in comparing reactions, liberates 48,800 Cal. according to equation (1) and 68,000 Cal. according to equation (2). Since the heat of combination of one atom of oxygen in the ferroso-ferric oxide produced by roasting spathic iron ore is 66,200 Cal., and is as much in ferric or ferrous oxides, the heat of reaction (2), but not of reaction (1), is just sufficient to reduce these oxides. In this way the action of carbon monoxide in the blast furnace could be explained by purely thermochemical data. But this explanation would fail completely in the reduction of oxides of baser metals, which can only be effected by reaction (3), thus :—



Considerable heat must therefore be absorbed from the surroundings for these reactions to proceed, and on this account they take place at high temperatures. The changes in the heats of formation with temperature are too small to expect that they would be reversed, and in fact the heat of formation of the reaction between carbon and zinc oxide at, for example,  $1000^\circ$  is still 55,000 Cal.

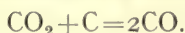
Even at the highest temperatures these reactions proceed with absorption of heat. If they are to take place at all the condition must be fulfilled which governs the occurrence of any reaction, the amount of free energy must decrease in it, i.e., in this case, the free energy which disappears in the formation of carbon monoxide must be greater than that which disappears in the formation of zinc oxide. At low temperatures, especially at absolute zero, when the heat of formation coincides with the energy of formation, the free energy gradient in the formation of zinc oxide is about three times as much as of carbon monoxide. Therefore in this and other cases the free energy gradient in the formation of the oxides of carbon and other elements must change considerably with temperature whether both decrease to a different extent or only one decreases or the free energy gradient of carbon monoxide increases.

We will now attempt to calculate the free energy gradient in

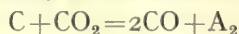
the formation of some technically important oxides, on the basis of these data.\* We will calculate first the energy of formation of

### Carbon Dioxide.

From the experiments of Deville † we know the equilibrium-constant at any given temperature of the reaction between carbon dioxide, carbon monoxide, and oxygen, i.e. the affinity  $A_1$  of the reaction  $2\text{CO} + \text{O}_2 = 2\text{CO}_2 + A_1$ . It is further known that the reduction of carbon dioxide to carbon monoxide by treatment with red-hot charcoal is not complete.‡



We can find the free energy gradient or affinity  $A_2$  of the reaction



at any given temperature by quantitatively establishing the equilibrium between carbon monoxide and carbon dioxide and solid carbon at that temperature. By the addition of both energy equations we obtain indirectly the affinity of the combustion of carbon,  $A_1 + A_2$

$$\text{C} + \text{O}_2 = \text{CO}_2 + A_1 + A_2.$$

According to Boudouard, § 99.3 per cent CO and 0.7 per cent  $\text{CO}_2$  coexist with solid amorphous carbon at  $1000^\circ$  and at atmospheric pressure. From the experiments of Deville || the degree of dissociation for one molecule  $\text{CO}_2$  at  $1000^\circ$  can be calculated to be about 0.0005. The oxygen  $y$  which is present together with carbon monoxide at 0.993 atmo. and carbon dioxide at 0.007 atmo. is obtained according to the law of mass action from the equations

$$\begin{aligned} K \cdot (1)^2 &= (0.0005)^2 \cdot (0.00025), \\ K(0.007)^2 &= (0.993)^2 \cdot y, \\ y &= (0.0005)^2 \cdot (0.00025) \cdot \frac{(0.007)^2}{(0.993)^2}, \\ y &= 3 \cdot 1 \times 10^{-15} \text{ atmo.} \end{aligned}$$

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\* It may be noted here that numerous and often contradictory data are to be found in the literature. Some only of these have been chosen to illustrate the method of calculation.

† According to Deville (*Ann. Chim. Pharmac.*, **134**, 124, **135**, 94), the degree of dissociation of carbon dioxide at  $3000^\circ$ ,  $\frac{\text{CO}}{\text{CO} + \text{CO}_2} = 0.4 \therefore k = \frac{0.6}{0.4 \times 0.4} = 3.67$  at  $3000^\circ$ .

‡ Ratke, *Abh. d. Naturf. Ges. zu Halle a. S.*, **15**, 1881; *Beibl. z. Wied. Ann.*, **5**, 183.

§ *Compt. rend.*, **128**, 842. *Bull. Soc. Chim.*, 5 Aug., 1899, and 5 March, 1900.  
|| *Loc. cit.* †



To combine solid carbon reversibly with oxygen at atmospheric pressure, we can take the equilibrium ascertained by Boudouard and introduce oxygen and remove carbon dioxide as in the cyclical process given on page 13. This gives the required affinity  $A_1 + A_2 = A$ ,

$$A = RT \ln \frac{1}{y} - RT \frac{1}{0.007},$$

or introducing the values

$$T = 1273, R = 1.99, y = 3.1 \times 10^{-15},$$

and the reduction factor 2.3 of natural logarithms to ordinary logarithms,

$$A = 4.58 \times 1273 \log. \frac{0.007}{3.1 \times 10^{-15}} = 72,010.$$

From the value 72,010 Cal. for the free energy  $A_{(C, O_2)}$  at  $1000^\circ \text{C.} = 1273^\circ \text{abs.}$ , the free energy  $A_{(C, O_2)}$  at any temperature can be readily calculated. In the formula which has been given for the free energy  $A_T = Q_O - aT \cdot \ln T - \beta T^2 + BT + RT \cdot \ln K$

assuming that oxygen at atmospheric pressure is transformed into carbon dioxide at atmospheric pressure,  $RT \cdot \ln K = 0$ . As the difference in specific heat of the substances vanishing and resulting, we have for the vanishing (reacting) substances:—

$$\text{Specific heat of } O_2 = 6.8 + 0T \text{ (p. 9)}$$

$$\begin{array}{l} \text{,,} \quad \text{,,} \quad C = 0 + 0.0077T \text{ according to Jüptner *;} \\ \quad \quad \quad \underline{C_r = 6.8 + 0.0077T} \end{array}$$

and for the substances produced:—

$$\text{Specific heat of } CO_2 = 6.8 + 0.0036T.$$

$$\therefore a + \beta T = +0.0041T \text{ (by subtraction).}$$

Therefore in the above equation  $a = 0$ ,  $\beta = 0.0041$ . Since the heat of combustion at ordinary temperature ( $301^\circ \text{abs.}$ ) is 97,650 Cal., at absolute zero it is

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\* There are difficulties in connection with the specific heat of carbon, since that of amorphous carbon is not sufficiently well known. H. Le Chatelier gives the expression  $1.92 + 0.0077t$  for the molecular heat of retort carbon between  $0^\circ$  and  $250^\circ \text{C.}$  Assuming that this holds to absolute zero, we have

$$1.92 - 0.0077 \times 273 + 0.0077T = -0.18 + 0.0077T,$$

which would give a value for the specific heat at absolute zero which would be negative, though small. This is impossible, so that we will follow the assumption of H. von Jüptner and take the specific heat of carbon as approximately  $C = 0.0077T$  (*Z. f. anorg. Chemie*, 1904, **39**, 58).

$$Q_O = Q_T - (a + \beta T)T \text{ (cf. p. 29)}$$

$$= 97,650 - 372 = 97,278.$$

To determine the thermodynamic unknown quantity B, the value 72,010 at  $1000^\circ = 1273^\circ$  abs. is inserted into the above equation for A,

$$A_{1273^\circ} = 72,010 = 97,278 - 0.0041 \times (1273)^2 + B.1273,$$

from which  $B = -14.63$ .

Therefore if oxygen at atmospheric pressure is transformed into carbon dioxide at atmospheric pressure we have for the free energy gradient at any temperature

$$A_{(C, O_2)} = 97,278 - 14.63T - 0.0041T^2.$$

However, if the oxygen is not at atmospheric pressure, but at the partial pressure  $p_{O_2}$  atmo., the energy gained is increased by the work which would be obtained in the expansion of the gas to atmospheric pressure, i.e. by  $RT \ln p_{O_2}$ , while this energy will be lowered by  $RT \ln p_{CO_2}$  if the partial pressure of the carbon dioxide is  $p_{CO_2}$  atmos. We therefore obtain for the free energy gradient of carbon dioxide

$$A_{(C, O_2)} = 97,278 - 14.63T - 0.0041T^2 + 4.58T. \log. \frac{p_{O_2}}{p_{CO_2}}.$$

Thus at high temperatures the energy of the reduction of carbon changes considerably. Further, the energy of reaction varies with the concentration of the carbon dioxide in the gaseous products of the combustion, and the smaller this is the higher is the energy of reduction. The energy of formation of carbon monoxide can be calculated from these data. Work is gained by expanding one mole of oxygen from atmospheric pressure to the pressure at which oxygen, carbon, and carbon monoxide are in equilibrium, and work is consumed by compressing two moles of carbon monoxide from the equilibrium pressure to atmospheric pressure. Since at equilibrium the formation of carbon monoxide takes place without work, the free energy gradient of two moles of carbon monoxide is obtained from the difference between the work gained and consumed. Therefore for the formation of one mole of carbon monoxide

$$A = \frac{1}{2}RT \ln \frac{1}{3.1 \times 10^{-15}} - RT \ln \frac{1}{0.993}.$$

$R = 1.99$  and  $T = 1273^\circ$ , so that after transforming into ordinary logarithms,

$$A_{T(C, \frac{1}{2}O_2)} = 2.29 \times 1273 \log. \frac{0.993^2}{3.1 \times 10^{-15}} = 42,560 \text{ Cal.}$$

As in the case of carbon dioxide, the difference in specific heat of the substances vanishing and those produced is:—

$$\begin{array}{rcl} \text{Specific heat of } \frac{1}{2}O_2 & = & 3.4 \\ \text{,, ,, C} & = & 0 + 0.0077T \\ \text{Sum} & = & 3.4 + 0.0077T \\ \text{Specific heat of CO} & = & 6.8 \\ \hline C_r - C_p & = & -3.4 + 0.0077T \end{array}$$

So that in this case  $\alpha = -3.4$ ,  $\beta = 0.0077$ , and  $Q_T = 29,650$ ,

$$\therefore Q_O = 29,650 + 3.4T - 0.0077T^2 = 29,988 \text{ Cal.}$$

The value of  $B$  is obtained in the same way:—

$$B = \frac{A_T}{T} - \frac{Q_O}{T} + \alpha \times 2.3 \log. T + \beta T,$$

$$\therefore B = \frac{42,560}{1273} - \frac{29,988}{1273} + 3.4 \times 2.3 \log. 1273 + 0.0077 \times 1273 = -4.61.$$

The free energy gradient for the formation of CO at a given temperature (all gases at 1 atmo.) is thus:—

$$A_{T(C, \frac{1}{2}O_2)} = 29,988 + 3.4T \ln T - 0.0077T^2 - 4.61T.$$

If the oxygen is at the partial pressure  $p_{O_2}$ , then the energy which can be gained is increased by

$$\frac{1}{2}RT \ln p_{O_2} = 2.29T \log. p_{O_2}$$

for each gram-molecule, and it is lowered by  $4.58 \log p_{CO}$  for each gram-molecule CO at the pressure  $p_{CO}$ . Thus the general equation is

$$\begin{aligned} A_{T(C, \frac{1}{2}O_2)} &= 29,988 + 3.4 \times 2.3T \log. T - 0.0077T^2 - 4.61T \\ &\quad + 2.29T \log. \frac{p_{O_2}}{p_{CO}^2}. \end{aligned}$$

Thus we see that the energy of formation of carbon monoxide increases with rise in temperature. Thus a compound produced with the evolution of heat need not be more unstable on increasing the temperature, but can increase in stability.

### Producer Gas.

We have already discussed in the last section the practical significance of producer gas for heating purposes and for driving gas-engines. Producer gas, which in the ideal case should consist of pure carbon monoxide, is made by incomplete combustion of coke by the oxygen of the air. We shall see that in making producer gas the highest possible working temperature must be selected to keep back the formation of carbon dioxide. According to the results of Ost the temperature of white-hot coal is recommended to obtain a practical and efficient producer gas. Therefore the manufacture of producer gas is theoretically a reduction of carbon dioxide by glowing charcoal. The theoretical discussion of the formation of producer gas involves a knowledge of the reaction  $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ .

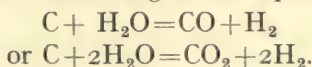
The free energy gradient of this reaction, the formation of carbon monoxide from carbon dioxide and carbon, is obtained from the difference between the free energy gradients  $2A_{\text{T}}(\text{CO}, \frac{1}{2}\text{O}_2)$  and  $A_{\text{T}}(\text{C}, \text{O}_2)$ .

$$\begin{aligned}
 2A_{\text{T}}(\text{CO}, \frac{1}{2}\text{O}_2) &= 59.976 + 6.8 \times 2.3T \log. T - 0.0154T^2 - 9.22T \\
 &\quad + 4.58T \log. \frac{P_{\text{O}_2}}{P^2(\text{C})} + 0.0041T^2 + 14.63T - 4.58T \log. \frac{P_{\text{O}_2}}{P_{\text{CO}_2}} \\
 -A_{\text{T}}(\text{C}, \text{O}_2) &= -97,278 \\
 \hline
 A_{\text{T}}(\text{CO}_2, \text{C}) &= -37.302 + 6.8 \times 2.3T \log. T - 0.0113T^2 + 5.41T \\
 &\quad + 4.58T \log. \frac{P_{\text{CO}_2}}{P^2\text{CO}}
 \end{aligned}$$

Apart from the influence of the partial pressure, below about  $930^\circ \text{ abs.} = 657^\circ \text{ C.}$  calculation shows that the free energy gradient is negative, i.e. the decomposition of carbon monoxide into carbon dioxide preponderates, while above this temperature the important reaction for the formation of producer gas takes place, the reduction of carbon dioxide by carbon. For, at  $930^\circ \text{ abs.}$ ,  $A_{\text{T}}(\text{CO}_2, \text{C})$  is already positive  $= (-37.302 + 37.457) \equiv +155$ .



Therefore, in practice, to obtain a producer gas of the highest possible calorific power, i.e. of the highest content in carbon monoxide, the highest possible temperature of reaction must be chosen. This reaction also plays an important part in the manufacture of heating gas by formation of water gas, i.e. by the reduction of water according to the equation



The water gas produced according to the first equation is the ideal water gas. Practice has shown that the first reaction mainly occurs at high, and the second at low temperatures, but at the same time it has been found that some carbon dioxide is obtained even when working at the highest temperatures. We will now consider these reactions theoretically, and we will see that theory and practice agree completely.

A knowledge of the free energy gradient in the formation of water vapour is necessary to calculate that in the reduction of water by carbon. This is given by the general formula

$$A_T = Q_O - a \times 2.3T \log. T - \beta T^2 + BT + 4.58 \log. \frac{P_A \cdot P_B}{P_C \cdot P_D}.$$

For permanent gases the mean  
specific heat at constant pressure is  $\text{H}_2 = 6.8$   
 $\frac{1}{2}\text{O}_2 = 3.4$   
10.2

This is diminished by that of the  
gases which disappear (one mole-  
cule  $\text{H}_2\text{O}$ ). Haber gives for steam  $8.35 - 0.00165T$   
 $\therefore a + \beta T = c_{(\text{H}_2 + \frac{1}{2}\text{O}_2)} - c_{(\text{H}_2\text{O})} = 1.85 - 0.00165T$   
therefore  $a = 1.85$ ,  $\beta = -0.00165$ .

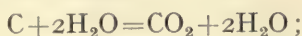
The heat of combustion of water at room temperature ( $T = 291^\circ$ ),  
 $Q_{291} = 58,000 \text{ Cal.}$

$$Q_O = Q_T - (1.85 - 0.00165T)T = 57,600.$$

The constant  $B = -2.28$  (Haber). Therefore

$$\begin{aligned} A_{T(\text{H}_2\text{O})} &= 57,600 - 1.85 \times 2.3T \log. T + 0.00165T^2 - 2.28T \\ &\quad + 4.58T \log. \frac{P_{\text{H}_2} \cdot P^{\frac{1}{2}}_{\text{O}_2}}{P_{\text{H}_2\text{O}}}. \end{aligned}$$

From the difference between the energy of formation of one mole carbon dioxide and two moles water, we obtain the free energy gradient of the reaction



$$\text{thus } A_{\text{T}(\text{C}, 2\text{H}_2\text{O})} = A_{\text{T}(\text{C}, \text{O}_2)} - 2A_{\text{T}(\text{H}_2, \frac{1}{2}\text{O}_2)},$$

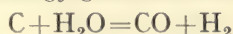
$$\begin{aligned} A_{\text{T}(\text{C}, \text{O}_2)} &= 97,278 - 14.63T - 0.0041T^2 + 4.58T \log. \frac{P_{\text{O}_2}}{P_{\text{CO}_2}} - \\ - 2A_{\text{T}(\text{H}_2\text{O})} &= -115,200 + 4.56T - 0.0033T^2 - 4.58T \log. \frac{P_{\text{H}_2}^2 \cdot P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} \\ &\quad + 4.6 \times 1.85T \log. T \end{aligned}$$


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$$A_{\text{T}(\text{C}, 2\text{H}_2\text{O})} = -17,922 - 10.07T - 0.0074T^2$$

$$+ 4.58T \log. \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 \cdot P_{\text{CO}_2}} + 4.6 \times 1.85T \log. T.$$

Analogously, the free energy gradient of the reaction



is obtained from the difference between that of the formation of carbon monoxide and steam,

$$A_{\text{T}(\text{C}, \text{H}_2\text{O})} = A_{\text{T}(\text{C}, \frac{1}{2}\text{O}_2)} - A_{\text{T}(\text{H}_2, \frac{1}{2}\text{O}_2)},$$

$$A_{\text{T}(\text{CO})} = 29,988 + 3.4 \times 2.3T \log. T - 4.61T + 4.58T \log. \frac{P_{\text{O}_2}^{\frac{1}{2}}}{P_{\text{CO}}}$$

$$- 0.0077T^2$$

$$- A_{\text{T}(\text{H}_2\text{O})} = -57,600 + 1.85 \times 2.3T \log. T + 2.28T$$

$$- 4.58T \log. \frac{P_{\text{H}_2} \cdot P_{\text{O}_2}^{\frac{1}{2}}}{P_{\text{H}_2\text{O}}} - 0.00165T^2$$


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$$A_{\text{T}(\text{C}, \text{H}_2\text{O})} = -27,612 + 5.25 \times 2.3T \log. T - 2.33T$$

$$+ 4.58T \log. \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \cdot P_{\text{CO}}} - 0.00935T^2.$$

Neither of the reactions in which water is reduced by carbon can occur at low temperatures, since they consume energy. When

the reaction takes place at a suitably high temperature a pure carbon dioxide water gas or carbon monoxide water gas can never be formed, but carbon dioxide, carbon monoxide, hydrogen, and steam will always coexist. For equilibrium to obtain, the free energy gradient of the carbon dioxide water gas must be equal to that of the carbon monoxide water gas, i.e.  $A_{T(C,2H_2O)} =$

$A_{T(C,H_2O)}$ , therefore

$$\begin{aligned} & -17,922 - 10.07T - 0.0074T^2 + 2 \times 1.85 \times 2.3T \log. T \\ & + 4.58T \log. \frac{P_{H_2O}^2}{P_{CO_2} \cdot P_{H_2}^2} \\ & = -27,612 - 2.33T - 0.00935T^2 + 5.25 \times 2.3T \log. T \\ & + 4.58T \log. \frac{P_{H_2O}}{P_{H_2} \cdot P_{CO}}, \end{aligned}$$

from which we obtain the following formula for the variation in composition of water gas with temperature:—

$$\begin{aligned} 9690 = & +7.74T + 1.55 \times 2.3T \log. T - 0.00195T^2 \\ & - 4.58 \log. \frac{P_{CO} \cdot P_{H_2O}}{P_{H_2} \cdot P_{CO_2}}. \end{aligned}$$

This shows that the greater the ratio of CO to CO<sub>2</sub>, the higher must be the temperature.

We can consider the reduction of zinc in a very similar way. This is effected by roasting the zinc blende found in nature, and thus transforming the sulphide to oxide. The residue essentially consists of the oxide and is admixed with coal and heated in closed vessels to 1200–1300°. The zinc escapes as vapour and is collected in suitable condensation apparatus.

The heat of formation, and thus at  $-273^\circ$  the free energy gradient of formation, of zinc oxide is 85,800 Cal. If it maintained this free energy gradient at higher temperatures it could not be reduced by carbon monoxide or by carbon giving carbon dioxide. The only reduction possible would be by carbon giving carbon monoxide, but a temperature of about 6000° would be required, which is not in agreement with practical experience. Boudouard \*

\* *Ann. d. Chim. et d. phys.*, (7) 24, 76.

found that carbon did not reduce zinc oxide at  $1100^\circ$ , but did so appreciably at  $1125^\circ$ . Therefore at this temperature the free energy gradient of zinc oxide must be equal to that of carbon monoxide, i.e. according to the formula on p. 35,

$$A = 29,988 + 3.4 \times 2.3 \times 1398 \log. 1398 - 0.0077 \times 1398^2 \\ - 4.61 \times 1398 = 42,932 \text{ cal.},$$

assuming that the gaseous reaction-products are under atmospheric pressure. In this case the change in the free energy gradient explains the otherwise inexplicable power of reduction at comparatively low temperatures.

In the reduction of iron ores the production of metal is preceded by the reduction of the higher oxide. The experiments of Braithwaite\* show that oxygen combined with iron above the ferrous state is more loosely bound and is removed by carbon monoxide before the formation of metallic iron begins. The heat of formation of ferrous oxide is 64,600 Cal., according to Le Chatelier.† Since at about  $900^\circ$  ferrous oxide is in equilibrium with iron and a waste gas containing 24 per cent carbon monoxide and 12 per cent carbon dioxide, the free energy gradient of ferrous oxide is equal to that of the oxidation of carbon monoxide at this temperature.

The free energy gradient of the oxidation of carbon monoxide to dioxide is obtained from the difference in free energy gradient of carbon dioxide  $A_{T(C,O_2)}$  and of carbon monoxide  $A_{T(C,\frac{1}{2}O_2)}$  :—

$$A_{T(C,O_2)} = 97,278 - 14.63T - 0.0041T^2 + 4.58T \log. \frac{P_{O_2}}{P_{CO_2}} \\ - A_{T(C,\frac{1}{2}O_2)} = -29,988 + 4.61T + 0.0077T^2 - 2.29T \log. \frac{P_{O_2}}{P^2_{CO}} \\ - 3.4 \times 2.3T \log. T \\ \hline A_{T(CO,\frac{1}{2}O_2)} = 67,290 - 3.4 \times 2.3T \log. T - 10.02T + 0.0036T^2 \\ + 2.29T \log. \frac{P_{O_2} \cdot P^2_{CO}}{P^2_{CO_2}}.$$

\* *Chem. News*, 1895, **72**, 211.

† *Compt. rend.*, 1895, **120**, 623.



Therefore for  $900^{\circ} = 1173^{\circ}$  abs.,

$$A_{T(\text{CO}, \frac{1}{2}\text{O}_2)} = 67,290 - 3.4 \times 1173 \times 2.3 \log. 1173 - 10.02 \times 1173 \\ + 0.0036 \times 1173^2 + 2.29 \times 1173 \log. \frac{0.24^2}{0.12^2} = 33,221 \text{ Cal.}$$

As a very rough approximation the change in the free energy gradient of ferrous oxide with temperature can be expressed by the following formula :—

$$A_{T(\text{Fe}, \frac{1}{2}\text{O}_2)} = 64,600 - \frac{64,600 - 33,221}{1173} T + 2.29 T \log. p_{\text{O}_2} \\ = 64,600 - 26.8 T + 2.29 T \log. p_{\text{O}_2},$$

which appears legitimate if we do not wish to obtain accurate figures, but merely to follow the course of the reaction. Then there is an equilibrium between iron, ferrous oxide, and carbon dioxide, when  $A_{T(\text{Fe}, \frac{1}{2}\text{O}_2)} = A_{T(\text{CO}, \frac{1}{2}\text{O}_2)}$ , i.e. when

$$64,600 - 26.8 T = 67,290 - 3.4 \times 2.3 T \log. T - 10.02 T + 0.0036 T^2 \\ + 4.58 T \log. \frac{\text{CO}}{\text{CO}_2},$$

$$\text{or } 4.58 \log. \frac{\text{CO}}{\text{CO}_2} = 3.4 \times 2.3 \log. T - 16.78 - 0.0036 T - \frac{2690}{T}.$$

This equation tells us that on raising the temperature the ratio of carbon monoxide to dioxide at equilibrium increases. This agrees well with the experiments of Bell,\* who found for the composition of the gaseous mixture :—

At white heat . . . . . 90% CO and 10% CO<sub>2</sub>.

At bright red heat . . . . . 68 „ „ 32 „

At dark red heat . . . . . 40 „ „ 60 „

While the free energy gradient of ferrous oxide decreases as the temperature rises, that of carbon monoxide increases. At rather a high temperature, estimated at about  $1400^{\circ}$ , the two free energy gradients become equal, and at higher temperatures the free energy gradient of carbon monoxide becomes greater; this serves to explain the reaction in the Bessemer process.

By blowing air through molten iron at about  $1300$ – $1500^{\circ}$  the

\* Wedding, *Handbuch der Eisenhüttenkunde*, p. 994.

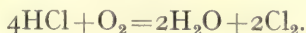
impurities of the iron are burnt, silicon, manganese, phosphorus, and especially carbon, and the iron is turned into metal which can be wrought. The fact that only carbon and not iron is oxidised in the Bessemer converter depends on the free energy gradient of carbon monoxide (and of the oxides of the other impurities mentioned) becoming greater than that of ferrous oxide with rising temperature. But it is known that the carbon cannot be completely removed without oxidising part of the iron. There are two reasons for this :—

- (1) There is not a complete equilibrium since, although the iron yields less free energy on oxidation, yet its large amount causes this oxidation to take place more rapidly than that of the small amount of carbon.
- (2) As we shall see later (V, 6) the carbon is present, partially at least, as carbide, for the oxidation of which an essentially higher amount of energy is required.

After these reduction processes we may consider an oxidation.

#### The Deacon Process

for obtaining chlorine depends on the oxidation of hydrochloric acid gas by atmospheric oxygen.



The free energy gradient in the formation of hydrochloric acid is 22,428 Cal. at 30°, from the measurements of Dolezalek \* on the E.M.F. of hydrochloric acid cells; it only increases very slightly with temperature. Haber † gives for the free energy gradient of hydrochloric acid

$$A_{\text{T(HCl)}} = 22,000 + 1.34T + 4.58T \log. \frac{P_{\text{Cl}_2}^{\frac{1}{2}} \cdot P_{\text{H}_2}^{\frac{1}{2}}}{P_{\text{HCl}}}.$$

The free energy gradient of the reaction on which the Deacon process is based is given by the difference between the free energy gradients of two moles of water and four moles of hydrochloric acid, thus :—

\* *Zeit. physik. Chemie*, **26**, 321.

† *Op. cit.*

$$\begin{aligned}
2A_{T(H_2O)} &= 115,300 - 3.7 \times 2.3T \log. T + 0.0033T^2 \\
&\quad + 4.58T \log. \frac{P_{H_2}^2 \cdot P_{O_2}}{P_{H_2O}^2} - 4.56T \\
-4A_{T(HCl)} &= -88,000 - 4.58T \log. \frac{P_{H_2}^2 \cdot P_{Cl_2}^2}{P_{HCl}^4} - 5.36T \\
\hline
A_{T(Cl_2, 2H_2O)} &= 27,300 - 3.7 \times 2.3T \log. T + 0.0033T^2 \\
&\quad + 4.58T \log. \frac{P_{O_2} \cdot P_{HCl}^4}{P_{Cl_2}^2 \cdot P_{H_2O}^2} - 9.92T.
\end{aligned}$$

At equilibrium the free energy gradient = 0, and we obtain, dividing by T,

$$4.58 \log. \frac{P_{O_2} \cdot P_{HCl}^4}{P_{H_2O}^2 \cdot P_{Cl_2}^2} = 3.7 \times 2.3 \log. T + 9.92 - 0.0033T - \frac{27,300}{T}$$

The greater T is, the greater is the value of the expression on the left-hand side, the higher is the concentration of hydrochloric acid at which the reaction comes to a stop, the more incomplete it is, and the smaller is the yield of chlorine obtained. Thus to obtain a good yield of chlorine the temperature must be kept very low. But at low temperatures the reaction-velocity is very small, and we thus find there is a conflict between the two technical requirements, completeness, and highest possible reaction-velocity. Accordingly a compromise must be made and an optimum temperature sought. However, even at such an intermediate temperature the reaction-velocity is still too small to give results which are good technically, and we have to increase the reaction-velocity by means other than raising the temperature. This can be done by the presence of certain substances (cupric chloride in the Deacon process) which have the power of increasing the reaction-velocity without influencing the free energy gradient. Such substances are termed catalytes. We shall see later that for the reaction  $SO_2 + O \rightarrow SO_3$  similar conditions hold as for the Deacon process. The fact that this reaction is catalytically accelerated by platinum sponge has been of

great importance in the development of the contact process for sulphuric acid, which is based on it.

Catalytes are very important in these and many other technical reactions, and therefore we will discuss the theory and application of catalytes in technical reactions before considering the practical consequences arising from the law of mass action as applied to the Deacon and contact sulphuric acid processes. We will devote the next chapter to catalytes, although they will also receive mention later.



## CHAPTER II

### REACTION-VELOCITY AND CATALYTES

#### 1. General Kinetic Considerations.

FROM what has been said as to the kinetic deduction of the law of mass action (p. 15), it is at once clear that at a definite temperature the reaction-velocity is proportional to the concentration of the reacting substances present at any moment. If their initial concentration is  $a$ ,  $b$ ,  $c$ , and if after time  $t$  the quantity  $x$  has reacted, then assuming that the reaction goes completely in one direction, the reaction-velocity  $\frac{dx}{dt}$  at time  $t$ , when only one substance  $a$  reacts, is given by :—

$$\frac{dx}{dt} = k(a-x) ;$$

if two substances  $a$  and  $b$  react, we have

$$\frac{dx}{dt} = k(a-x)(b-x) ;$$

and if three substances  $a$ ,  $b$ , and  $c$  react, we have

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) ;$$

and so on.

$k$  is a constant which is only dependent on the temperature and on the nature of the reacting substances ; it is the characteristic constant number which defines the reaction-velocity of a given reaction, while  $\frac{dx}{dt}$  continually changes.

As will be seen from the above formulæ,  $\frac{dx}{dt}$  is large at the beginning of a reaction when the concentration of the reacting substances is high. As the reaction proceeds,  $\frac{dx}{dt}$  becomes smaller

and smaller, i.e. the final state is reached after 10–20 times as long as the half-way state, which is a fact of undoubted technical interest. The decrease in the value of  $\frac{dx}{dt}$  is the greater the more substances react with one another. According to the number of the reacting substances the reaction is termed mono-, bi-, tri-molecular. It should be noted that the latter are rare, and in most cases, when more than two substances react, the reaction is really bi-molecular, since the observed total reaction proceeds by stages as several bi-molecular partial reactions (cf. Hydrolysis of Fats, cap. VII, 5).

While in mono-molecular reactions the velocity  $\frac{dx}{dt}$  is independent of the concentration of the reacting substances, in bi-molecular reactions it is inversely proportional to the concentration, and in tri-molecular reactions inversely proportional to the square of the concentration. This fact is frequently of technical interest when it is desired to increase the velocity of a reaction by raising the concentration only. Another means of increasing the reaction-velocity is to raise the temperature. All quantitative experiments have shown that the velocity with which a chemical system proceeds to its state of equilibrium increases extraordinarily with rising temperature. Usually an increase of temperature of 10° approximately doubles the reaction-velocity. In many cases, however, the influence of temperature is larger or smaller.

We may consider the reaction-velocity, like the movement of a material point in a highly viscous medium, as the effect of the interaction of two opposite factors—in this case chemical force and chemical resistance. We may write :—

$$\text{Reaction-velocity} = \frac{\text{Chemical force}}{\text{Chemical resistance}}.$$

The reaction-velocity may, therefore, be increased either by increasing the chemical force or by decreasing the chemical resistance. Though rise of temperature increases the chemical force of many processes in consequence of the increase of energy, the accelerating action of temperature is also due to diminution of chemical resistance, just as viscosity is decreased by rise of temperature. But as we have seen in the case of the Deacon

process, an increase of temperature is often injurious in technical processes apart from the high cost of heating, i.e. it is unfavourable for the yield in technical working. Thus we must find other means to diminish the chemical resistance of such reactions. Catalytes are extremely useful in this connection.

## 2. Catalytes in General.

The essential feature of a catalyte is that it raises or, generally, changes the velocity of a chemical reaction by its mere presence without its having undergone any change when the reaction is over. It is characteristic of a catalyte that its amount is small compared to that of the reacting substances. On this account the catalyte will never induce a reaction, but will only accelerate or change the reaction-velocity of reactions which proceed spontaneously, i.e. with a decrease of free energy. Thus if we call a substance a catalyte we mean that it should never act in the direction of increasing or decreasing the energy, i.e. it should only influence the chemical resistance, but not the driving force of a reaction. It follows as a necessary consequence that if a catalyte influences the velocity of one reaction leading to an equilibrium, it must also influence, in the same direction and amount, the second opposite reaction which leads to equilibrium. For, if this were not the case, the equilibrium-constant  $K$  in the equation

$$K = \frac{k_1}{k_2} \quad (\text{p. 15})$$
would be changed, which would imply a change of energy, thus contradicting the above definition of a catalyte. Thus a catalyte can never *induce* a chemical reaction, but can only accelerate reactions which proceed spontaneously with a small, often infinitely small, velocity, or can retard a reaction which proceeds rapidly. Catalytes are distinguished as positive or negative, according as to whether they raise or lower the velocity of a chemical reaction. Acids, or more correctly the  $H^+$  ions split off from them, accelerate the inversion of cane sugar, while certain polyvalent higher alcohols retard the oxidation of alkali sulphites to sulphates by atmospheric oxygen. Cases can also occur in which the catalytic action of a catalyte is influenced by a second catalyte, whose amount again only requires to be small in comparison to that of the first catalyte. Such substances are called anti-catalytes. The classical and technically important example is the retarding action exerted by small quantities of

arsenic acid on the catalytic accelerating action of spongy platinum in the combination of  $\text{SO}_2$  and  $\text{O}$  to  $\text{SO}_3$ . When the contact process for sulphuric acid was first introduced, the platinum asbestos used as catalyte became inactive after a short time through small quantities of arsenic acid which were contained in the sulphurous acid obtained by roasting arsenical pyrites. This anti-catalyte threatened to ruin the rising industry, until arsenic acid was recognised as the anti-catalyte which caused the inactivity of the catalyte, and the sulphur dioxide used was made free from arsenic.

Auto-catalysis is an important special case of catalysis in which the typical phenomenon is that one of the reaction-products acts as a catalyte. Since in general, at least as a first approximation, the activity of catalytes is proportional to their concentration, in the case of auto-catalysis the reaction-velocity steadily rises as the reaction proceeds. A third substance may catalytically accelerate the origination of such an auto-catalyte, but may not itself catalytically accelerate the main reaction. Such substances are called pseudo-catalytes.

There is a further series of substances which accelerate reactions partly or wholly by supplying energy, i.e. by increasing the driving force. This holds especially in cases where the acceleration is only effected by rather large quantities of these substances, e.g. the presence of sulphuric acid in the preparation of nitroglycerine,



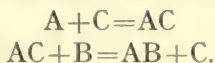
According to our definition given above the latter substances are not true catalytes, but in many cases it is difficult to draw the line between the two classes. The substances now in question are also of technical importance, and examples will be mentioned later; we will call them *ad hoc* "false catalytes."

Before considering the technically important cases in which a part is played by catalytes, pseudo-catalytes, and false catalytes, we must briefly discuss the three more important theories which attempt to explain catalytic phenomena. At this point we may note that it seems practically impossible to formulate a theory which is universally valid for all the various catalytic reactions. In the numerous and so essentially different cases of catalytic action we find that sometimes one theory appears correct, sometimes another.



### 3. The Theory of Intermediate Reactions. The Chamber Process and other Important Technical Reactions.

The oldest theory of catalytic action is that of the "intermediate reaction," which assumes quite generally that if a catalyte C accelerates a reaction  $A+B=AB$ , the action of the catalyte is to be explained by the fact that an intermediate body AC is formed, whose formation and decomposition into B proceed more rapidly than the direct reaction, i.e. the reaction  $A+B=AB$  proceeds more slowly than the two reactions



The catalytic acceleration of the oxidation of hydrochloric acid with permanganate due to the presence of chromium, cadmium, platinum, and ferrous salts is, in fact, a case in which it has been proved not only that an intermediate body is formed, but that this reacts more rapidly than the original bodies themselves. Experiment showed that the complex metal hydrochlorides which were formed decomposed more rapidly than HCl.

The important catalytic action of nitric oxide in the chamber process for the formation of sulphuric acid can be explained on this theory. It is known that nitric oxide can be oxidised and reduced very rapidly. Among the great variety of nitrogen compounds which are capable of existence in the presence of oxygen, water, and sulphuric acid and are easily changeable, it is difficult to decide which is the true carrier. The researches of M. Trautz\* render it probable that at all events formally we can speak of nitric oxide NO as catalyte, though the process is highly complicated. We will consider Trautz's researches somewhat more fully in connection with the theory of the chamber process. The

#### Chamber Process

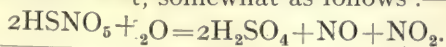
depends on the facts that a mixture of about 7 per cent  $SO_2$  with air, heated to about  $90-140^\circ$ , when passed over a solution of nitrosyl-sulphuric acid in sulphuric acid (67-76 per cent strength) in a Glover tower takes up nitric oxide, nitrogen dioxide, and water, and when passed through a series of chambers (lead chambers) deposits the sulphuric acid resulting from this mixture.

\* *Zeitschr. f. phys. Chem.*, **47**, 608,

This acid contains nitrosyl-sulphuric acid and is freed from it as far as practicable by addition of water in the chambers, as well as by the action of sulphur dioxide and differences of temperature. This is mainly effected by allowing it to run down the Glover tower. Excess of nitrogen dioxide, if desired mixed with nitric oxide, is held back in an absorption tower (Gay-Lussac tower) down which strong sulphuric acid trickles; the gas thus returns to the process. The fact that a great part of the sulphur dioxide is oxidised when this gas, mixed with an excess of oxygen or air and nitrogen dioxide,\* is passed through fairly dilute sulphuric acid, led to the construction of the Lunge-Rohrmann disc towers. In this process the gas mixture rises through apparatus provided with acid-resisting stones over which water is trickling. By this means the gases come in contact with acid which is already fairly concentrated, thus avoiding a phenomenon which also becomes inconveniently noticeable in the chambers if the acid is too dilute (under about 40 per cent acid), i.e. reduction of nitrogen dioxide and nitric oxide to nitrous oxide or nitrogen. This leads to rather large losses of nitrogen. If the acid produced in the chamber is too strong it cannot be so completely denitrated in the Glover tower, apart from the fact that it attacks the lead of the chamber. Both these phenomena occur to a small extent even in correct working.

It has been established by the researches of Lunge and Naef, Schertel and others, that even in the first chamber a sulphuric acid is deposited which is very rich in nitrosyl-sulphuric acid. Further, it is known that the concentration of the sulphuric acid in the chambers varies only from 55 to 65 per cent, and that the denitration of the chamber acid by dilution with cold or hot water or steam is only very incomplete. On the other hand, experiments made to employ the Glover tower as a production tower have shown that the zone of denitration produces 200 times as much as the same space in the chamber.†

The formation of sulphuric acid in the Glover tower and in the chambers results through the decomposition of the nitrosyl-sulphuric acid formed there, somewhat as follows:—



\* The nitrogen dioxide for this purpose is made from nitric acid or sodium nitrate. There is required about one-thirtieth of the amount, which alone would oxidise sulphur dioxide to sulphuric acid.

† [This is denied by some good authorities.—Tr.]

According to Trautz, in  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$  mixtures this reaction proceeds faster, the greater the concentration of the water, which is a necessary consequence of the equations deduced on page 15, since

$$\frac{dx}{dt} = k \cdot C_{\text{nitrosyl-sulphuric acid}} \cdot C_{\text{water}}.$$

The greater the concentration of the water the greater must be  $\frac{dx}{dt}$ . The smaller the concentration of the  $\text{H}_2\text{SO}_4$  and the greater the concentration of  $\text{HSNO}_5$ , the greater is the amount of  $\text{NO}_2$ , but in no case does the hydrolysis of nitrosyl-sulphuric acid take place in such a simple manner as above, and we have rather to deal here with the superposition of a series of single reactions. At the same time for a series of different mixtures of sulphuric acid and water Trautz obtained constant values for  $k$  in the formula

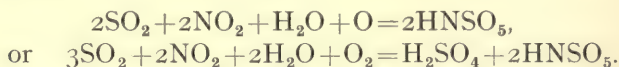
$$k = \frac{1}{t} \cdot \log. \frac{a}{(a-x)},$$

when  $a$  is the initial concentration, and  $x$  the amount of the nitrosyl-sulphuric acid which has been decomposed at time  $t$ . The concentration of the water is taken as constant on account of its very much higher value; consequently the reaction will take place as an apparently mono-molecular one. In very dilute mixtures of sulphuric acid and water, the hydrolysis takes place so rapidly that only the velocity of evolution of nitric oxide from the supersaturated solution is measured.

Trautz does not consider as correct the view put forward by Lunge and Sorel that formation and decomposition of nitrosyl-sulphuric acid proceed at different places in the chamber process, and are therefore determined by different concentration and temperature conditions; for, if this were the case, proportionately little acid would be produced in the Glover tower, since here the hydrolysis of the strong nitrosyl-sulphuric acid solutions is too small on account of the too small dilution, or more correctly on account of the varying concentration. Therefore in the Glover tower the greater part of the sulphuric acid must be produced otherwise than by local and separate formation and hydrolysis. Now out of many possible ways it appears most likely that



nitrosyl-sulphuric acid is simultaneously formed and decomposed at the same place, or that it passes through  $(\text{SO}_3\text{H})_2\text{NO}$ . The latter explanation has the advantage of accounting better for the simultaneous concentration and formation of sulphuric acid, the more so since the suitable concentration coincides with the lower concentrations in the Glover tower where denitration occurs. A similar explanation holds good for the chambers. Here also the differences in water concentration are proportionally small. We must agree with this newer theory with the reservation that nitrosyl-sulphuric acid is hydrolysed by rather weak sulphuric acid, not in the solid form, but already dissolved in strong sulphuric acid. Trautz attempted to decide the question of the formation of nitrosyl-sulphuric acid by experiments on its velocity of formation. He found that both under the conditions of the chamber and at ordinary temperatures, nitrosyl-sulphuric acid *instantly* results from  $\text{SO}_2$ , O, NO or  $\text{NO}_2$ , and a little water, while with more water a solution of nitrosyl-sulphuric acid is instantly produced, somewhat as follows :—

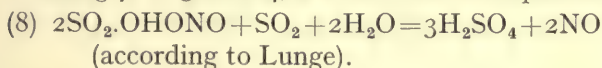


As Trautz showed, hydrolysis also leads to an equilibrium immeasurably fast. The question as to the intermediate existence of nitrosyl-sulphuric acid has not been decided, in so far as it cannot be established whether the main reaction is the direct one or the one with the intermediate stage. To formulate the theory of the chamber process provisionally, Trautz recommends that those reactions should be registered which can be proved to occur under chamber conditions, and that that theory should be preferred which allows as many as possible of the reactions, proved to take place, to be deduced from the fewest possible peculiarities of the substances under consideration. Trautz puts forward the following scheme for the reactions occurring in the chamber and in the Glover tower, taking into consideration the observation of Raschig that nitrogen compounds containing hydroxyl linked to nitrogen have the tendency to give condensation products with sulphuryl derivatives. All the following reactions proceed immeasurably fast: the simplest molecular coefficients have been taken.



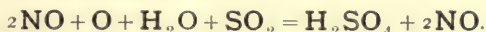
- (1)  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NO} \cdot \text{OH}$ .  
 (2)  $\text{NO} \cdot \text{OH} + \text{HSO}_3\text{H} \rightarrow 2\text{NOSO}_3\text{H}^* + 2\text{H}_2\text{O} \rightarrow$   
 $\text{NO} \cdot \text{OH} + \text{HSO}_3\text{H} \rightarrow$   
 (3)  $\rightarrow \text{NO} \begin{matrix} \text{SO}_3\text{H} \\ \text{SO}_3\text{H} \end{matrix} + \text{NO} + 2\text{H}_2\text{O}$ .  
 (4)  $\text{NO} \begin{matrix} \text{SO}_3\text{H} & \text{OHNO} \\ \text{SO}_3\text{H} & \text{OHNO} \end{matrix} \rightarrow 3\text{NO} + 2\text{H}_2\text{SO}_4$ .  
 (5)  $2\text{NO} + \text{O} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{NO}_2 \cdot \text{SO}_3\text{H} + \text{H}_2\text{O}$ .  
 (6)  $2\text{ONO} \cdot \text{SO}_3\text{H} + 2\text{H}_2\text{O} + \text{NO}(\text{SO}_3\text{H})_2 \rightarrow 4\text{H}_2\text{SO}_4 + 3\text{NO}$   
 quite analogous to 4.  
 (7)  $\text{ONO} \cdot \text{SO}_3\text{H} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{NO} \cdot \text{OH}$   
 (according to Lunge).

Combining 7, 2, 3, and 4, we have the net equation :—



Further,

(9)  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  (Lunge, Porschnew), giving as the total equation for the whole process :



Thus here NO is the catalyte which falls out from the net equation. It is still undecided whether besides the above reactions the following do not also take place, direct, as suggested by Lunge.

- (10)  $2\text{NO} + \text{H}_2\text{O} + 2\text{SO}_2 + 3\text{O} = 2\text{NO}_2 \cdot \text{SO}_3\text{H}$ .  
 (11)  $\text{SO}_2 + \text{HNO}_3 \text{ vapour} = \text{NO}_2 \cdot \text{SO}_3\text{H}$ .  
 (12)  $\text{SO}_2 + \text{NO} \cdot \text{OH} + \text{O} = \text{SO}_2\text{OHNO}_2$ .  
 (13)  $2\text{SO}_2 + \text{NO} + \text{NO}_2 + \text{O}_2 + \text{H}_2\text{O} = 2\text{NO}_2 \cdot \text{SO}_3\text{H}$ .  
 (14)  $2\text{SO}_2 + 2\text{NO}_2 + \text{O} + \text{H}_2\text{O} = 2\text{HSNO}_5$ .

According to Trautz, on account of the immeasurable velocity it is undecided which of the above reactions preponderate, and it is possible, indeed probable, that a large number of other unknown reactions may also occur. The cause of this is to be sought in the extraordinary variety of condensation products which are furnished by the acids of nitrogen with sulphuric acid.

The oxygen-carrying action of nitric oxide is technically useful in the chamber process, but this action may also prove incon-

\* Nitrososulphonic acid (quite hypothetical).

venient, as in the case of the preparation of nitro-glycerine and other explosives, when traces of nitrous acid cause excessively dangerous spontaneous decomposition of the explosive on account of the catalytic carrying of oxygen unless these traces are carefully removed from the product.

In the preparation of cyanides and thiocyanates and in Schloesing's method of transforming hydrochloric acid into chlorine, the reaction occurs by the alternate oxidation and reduction of nitrogen compounds. But in the latter process, as in the Weldon process, there is no pure catalytic transference of atmospheric oxygen, for external energy must be added; the reason is that the free energy gradient would be negative, when forming chlorine and water from oxygen and solutions of hydrochloric acid as dilute as are used in the Weldon and in the Schloesing process. In the latter, energy is added in the form of heat, to concentrate the nitric acid obtained in a dilute state in the regeneration, and to concentrate the solutions of manganese nitrate, and also in the decomposition of this salt into manganese peroxide and nitrogen dioxide.

The Weldon process depends on the evolution of chlorine from hydrochloric acid and pyrolusite :—

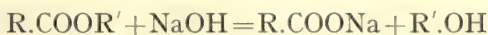


By treating the manganese chloride solution with lime a precipitate is obtained consisting of two molecules  $\text{Mn}(\text{OH})_2$  and one molecule  $\text{Ca}(\text{OH})_2$ , which is oxidised by blowing in air. The manganese peroxide and lime precipitate thus obtained is separated from the calcium chloride solution which flows away and this precipitate goes back to the process and thus in a certain way acts as oxygen carrier. Naturally the reaction with lime adds external energy, and this is a case of false catalysis. The Deacon process (p. 43) is a case of pure catalysis, in which the oxidation of the hydrochloric acid is effected by atmospheric oxygen alone with the intermediary of chlorides of copper. In the initial conditions of the Deacon process the free energy of formation of the hydrochloric acid gas is smaller than that of formation of water, and thus, in contradistinction to the earlier mentioned processes of Schloesing and Weldon, the decomposition of hydrochloric acid proceeds spontaneously, i.e. without addition of foreign energy, but the reaction cannot take place completely,

since the energy required for the decomposition of hydrochloric acid gas becomes greater the more dilute is the gas. Finally part of the hydrochloric acid must be again absorbed as such in water, and from the solution hydrochloric acid gas can be again obtained, e.g. by passing into concentrated sulphuric acid (Hasenclever). To transform the rest of the hydrochloric acid into chlorine it is necessary to add external energy, which is added in the form of heat when evaporating the sulphuric acid. Beyond cupric chloride the sulphate can also act as carrier; both salts are extremely sensitive to poisons (anti-catalytes, cf. p. 47). We will consider the technically important application of the law of mass action to the Deacon process in a separate chapter.

#### 4. Other Theories of Catalytic Phenomena. Euler's Theory and the Adsorption Theory.

According to Euler's theory the catalyte acts by increasing the concentration of the groups of ions reacting. Euler assumes that all reactions are ionic reactions. These are known to proceed with very great velocity, whenever the concentration of the ions is measurably great. The fact that ionisable substances, even when they act in non-aqueous solution or in the pure state, instantly exchange the atoms and atomic groups otherwise split off as ions, makes the use of catalytes unnecessary in the inorganic industries except when dealing with oxidation or reduction reactions. Euler's assumption is likewise not to be viewed as a general explanation of catalytic processes, but is only to be used in some cases for the explanation of catalytic action. Thus in general Euler's theory well explains the action of traces of moisture in catalytic reactions. For example the hydrolysis of esters



proceeds very rapidly in aqueous solution (for the hydrolysis of ethyl acetate at  $25^{\circ}$ ,  $k=6.4$ ); in absolute alcoholic solution the velocity of hydrolysis is about 1000 times smaller\*; small quantities of water cause an extraordinary acceleration of the velocity of hydrolysis—far more than would be calculated according to the law of mixtures. The addition of 5 per cent of water to an alcoholic solution raises the velocity of hydrolysis 30

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\* R. Kremann, *Monatsh. f. Chemie*, 1905, **26**, 279.



times. Again, the accelerating action of radium rays on the formation of water from an explosive oxygen-hydrogen mixture is explained by Edwards and Bergen on Euler's theory by the ionising action of radium rays on the reacting gases.

The third explanation of catalytic action is specially interesting from the technical standpoint. According to this theory the catalyte adsorbs the reacting substances, when the reaction-velocity is greater in the state of solid solution or of an adsorption compound than in the gaseous state. The experiments of Péan St. Gilles and Berthelot show that on passing from the gaseous to the liquid state or to that of solid solution the reaction-velocity does in fact increase, and conversely that when the reacting substances pass into the gaseous state there is observed under the same conditions a retardation of the reaction-velocity. According to these authors the velocity of esterification in the liquid state is about 1000 times greater than if the reacting substances, acid and alcohol, were in the gaseous state. Therefore the adsorption theory will be peculiarly applicable to the cases of gas reactions and dilute solutions in which the reaction is accelerated by a heterogeneous catalyte with a comparatively great surface.

Among reactions of this type, beyond the frequently mentioned Deacon process, the catalytic action of finely divided platinum on gas reactions is of special technical interest. A good example is the action of platinum in the Döbereiner lamp or, in its modern modification, the automatic gas lighter. In both cases owing to the increased reaction-velocity a local combination occurs on the platinum of atmospheric oxygen with the combustible gas flowing over the platinum (hydrogen, illuminating gas). Beyond the acceleration by the catalytic action of the platinum there is also an acceleration due to the rise in temperature owing to the heat of reaction which is liberated. The reaction-velocity thus rises by co-operative influences until finally a temperature is attained at which the gas mixture ignites. We may further refer to the catalytic action of platinum in the contact process for sulphuric acid, to which we will return in a later chapter. In connection with the above-mentioned explanation of the catalytic action of platinum as a surface action, it is important that instead of platinum in such gas reactions finely divided metals of the platinum group can be used, or ferric oxide or even smooth,



though preferably rough, fragments of porcelain. But the intensity of the catalytic activity diminishes from the platinum metals to ferric oxide and more so to rough fragments of porcelain, while the smooth fragments exert an action which, though unmistakable, is exceedingly small. Moreover, the adsorptive power of these catalytes for the reacting gases steadily decreases in the above series. Platinum also serves to carry atmospheric oxygen to methyl alcohol in the preparation of formaldehyde, and this cheap method has acquired great importance in the dye and leather industries, as well as for photography and disinfection. Platinum is used as a catalyte in the process proposed by Ostwald for the preparation of nitric acid or nitrates from ammonia. The activity of wood charcoal in the purification of alcohol is to be explained by surface action, whereby the oxidation of the fusel oils to acids and perhaps their esterification is catalytically accelerated. Surface action also explains the rapid oxidation of the organic matter contained in the effluent water of towns or works when this is filtered through coke which is then exposed to the air and acts as a carrier for the oxygen. Ferric oxide acts in the same manner as an oxygen carrier in the purification of sewage. According to Spring, catalytes also act in the self-purification of rivers by air and light. The activity of anti-catalytes can be well explained by the adsorption theory. Small quantities of sulphurous acid or dust prejudice the activity of the gas-lighter in the same way as small quantities of arsenic acid make the platinum inactive in the contact process for sulphuric acid. The fact that in comparison to the catalyte a considerably smaller quantity of the anti-catalyte can exert a retarding action is to be explained on the adsorption theory as signifying that even a small quantity of the anti-catalyte is enough to make the active surface of the catalyte inactive. The experiments of Bredig on the catalysis of hydrogen peroxide by platinum are especially suggestive for this explanation of anti-catalytic action. Hydrogen peroxide evolves oxygen by the catalytic action of platinum, but the same action is also exerted by many other foreign substances, such as dust, etc., which is technically important, since hydrogen peroxide is used for bleaching. Thus the bleacher has to take care that his hydrogen peroxide is not decomposed by catalytes.

Bredig examined the theory of the catalysis of hydrogen

peroxide and the poisonous action of other substances on the catalytic action of platinum. To obtain results which were always comparable, instead of spongy platinum he employed a so-called colloidal solution of platinum which was obtained by cathodic disintegration by an arc under water. We will now briefly discuss the nature of colloidal solutions.

### 5. Colloidal Solutions and the Catalytic Action of Colloidal Platinum.

In colloidal solutions we are dealing with a subdivision of a solid substance which is so fine that it is impossible to separate the solid from the liquid by the ordinary methods of mechanical separation (decantation, filtration). In contradistinction to true solutions, which are homogeneous systems containing only one phase, colloidal solutions are heterogeneous two-phase systems containing the suspensive liquid and ultra-microscopically small solid particles. This lack of homogeneity becomes evident on considering the optical properties of a colloidal solution. True solutions, such as those of sodium chloride, are optically empty, i.e. a beam of light passing through remains invisible in the interior of the liquid; in the interior of a colloidal liquid the path of the beam can be followed perfectly distinctly, as if it were in a dusty atmosphere. Further, colloidal solutions show no rise in boiling-point as do true solutions compared with the pure solvent just as the boiling-point of water is not influenced by a suspension of quartz sand. A special characteristic of colloidal solutions which is lacking in true solutions, is the phenomenon of coagulation. By addition of a definite quantity of electrolyte to colloidal solutions a separation can be effected of the ultra-microscopic particles from the suspensive liquid, since a filterable precipitate is then obtained. For any given colloidal solution, using a given electrolyte, there is a minimum addition which is necessary to separate the colloidal particles and the liquid maintaining them in suspension. This minimum depends on the stability of the colloid and on the nature of the electrolyte. For example a solution of colloidal ferric hydroxide is rendered turbid by a definite minimum addition of Glauber's salt, and the ferric hydroxide separates out as a compact precipitate which can then be filtered. An analogous phenomenon is the curdling of milk a colloidal solution of casein, by the addition of acid, or by the acid which results on souring. The colloidal particles of a solution

contain a certain amount of adsorbed water, and a state of equilibrium sets in between it and the solvent. If the solution contains an electrolyte of a concentration less than that corresponding to the limit of precipitation, the colloid adsorbs a more or less concentrated solution of electrolyte instead of pure water. If the solution contains several substances they will mutually influence one another and divide themselves in a definite ratio between solution and colloid.

We will now return to the colloidal solution of platinum (platinum sol). This acts somewhat like platinum sponge; only naturally in consequence of the enormously fine subdivision the active surface is considerably greater and is distributed so homogeneously in the reaction liquid that we can actually introduce the conception of the concentration of the catalyte. According to what has been said above the catalytic action of the colloidal platinum solution is explained by considering that the reacting substances present in the solution are adsorbed by the colloid, and can react faster in this somewhat more concentrated system than in the dilute solution. The catalytic action of colloidal platinum in the decomposition of hydrogen peroxide increases with rising quantities of platinum more rapidly than corresponds to a simple proportionality; this is to be explained by the undoubted heterogeneity of the catalyte, since the active surface increases more rapidly than the mass. Gold sol obtained in the same manner as platinum sol acts similarly, and one gram-atom of either of these colloidal metals in one million litres of water can still exert a marked accelerating action. There is quite a remarkable analogy between gold and platinum sols, and enzymes and blood, with respect to their property of being rendered inactive by small traces of certain poisons.

The retarding action on platinum catalysis is still very appreciable on addition of:—

| 0.0000001 gram-molecule | $\text{H}_2\text{S}$              | in 1 litre. |
|-------------------------|-----------------------------------|-------------|
| 0.00000005              | HCN                               | „ „         |
| 0.00000005              | KCN                               | „ „         |
| 0.0000001               | $\text{I}_2$                      | „ „         |
| 0.00004                 | $\text{Br}_2$                     | „ „         |
| 0.00004                 | $\text{NH}_2\text{OH}$            | „ „         |
| 0.00018                 | $\text{C}_6\text{H}_5\text{NH}_2$ | „ „         |
| 0.00004                 | $\text{P}_4$                      | „ „         |



|          |               |                                   |             |   |
|----------|---------------|-----------------------------------|-------------|---|
| 0.00024  | gram-molecule | $\text{PH}_3$                     | in 1 litre. |   |
| 0.001    | „             | $\text{C}_2\text{O}_4\text{H}_2$  | „           | „ |
| 0.000001 | „             | $\text{HgCl}_2$                   | „           | „ |
| 0.0048   | „             | $\text{HgCy}_2$                   | „           | „ |
| 0.002    | „             | $\text{Na}_2\text{SO}_3$          | „           | „ |
| 0.0002   | „             | $\text{Na}_2\text{S}_2\text{O}_3$ | „           | „ |
| 0.0003   | „             | $\text{HCl}$                      | „           | „ |

A very strong retarding action is also exerted by carbon monoxide, arsenuretted hydrogen, carbon bisulphide, and amyl nitrite which has become decomposed. Nitrous acid, pyrogallol, and arsenic acid are weaker, nitrobenzene, hydrofluoric acid, and ammonium fluoride still weaker, while potassium chlorate, sulphuric acid, nitric acid, ether, alcohol, glycerol, amyl alcohol, etc., have practically no action.

In the majority of cases there is an unmistakable agreement between the retarding action of the above "poisons" on ferment and blood catalysis on the one hand and on platinum catalysis on the other hand, though there are exceptions. Phenomena of recovery take place in the retardation of platinum catalysis by  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{P}$ ,  $\text{PH}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{NH}_2\text{OH}$ , etc., which can be easily explained by the ready oxidisability of these substances. There are analogies to this in the case of enzymes. The behaviour of  $\text{CO}$  is especially characteristic, and it is particularly interesting that platinum sol which has recovered from  $\text{CO}$  poisoning is much more active than before. As in enzymes, the order of addition of poison and  $\text{H}_2\text{O}_2$  to the catalyte has often a great influence on the strength of the retardation, which is further affected by the "time of incubation" of the poison with the platinum before adding the hydrogen peroxide.

All these facts point to a striking analogy between contact action in the inorganic world and ferment action in the organic world. The latter catalytes, those which have been used from antiquity, are still of the greatest technical importance. Their action is apparently in no case associated with the life process. Certain moulds or bacteria each yield as a product of growth a quite definite protein-like substance (ferment, enzyme), which itself exerts a quite definite catalytic action. We may explain the catalytic activity of these substances by considering them as colloidal solutions which are thus catalytically active by sur-



face action. Further, the life process of the animal organism depends upon the action of such ferments. The small amounts of poisons which retard the life process and can bring it to a standstill act as anti-catalytes, and we have seen that comparatively small quantities of these can make larger quantities of the catalyte inactive. It should be mentioned that those substances which we have found to be anti-catalytes in the catalysis of hydrogen peroxide are also poisons for numerous enzymes as well as for the human organism. We may note that research on the catalytic action of substances causing disease (anti-catalytes) has proved a great stimulus in chemical industry, and that the research methods of physical chemistry have afforded assistance of practical importance in the study of the catalytes of animal organisms, the toxins and antitoxins.

#### 6. The Catalytic Action of Ferments and of H and OH ions.

One of the oldest ferments is diastase, a growth-product of germinating grain, which has the power of rapidly bringing starch, especially in a pasty form, into solution with simultaneous hydrolysis, yielding maltose :



This saccharified starch is employed for the manufacture of alcohol or alcoholic drinks by using pure yeast cultures containing zymase as the active enzyme. Recently, instead of the yeast ferment, the mould ferment of Japanese Saké has been employed, which yields a ferment exerting the combined action of diastase and zymase, and therefore simultaneously saccharifying starch and fermenting the sugar so obtained. Two mould ferments (species of *Citromyces*) yield a ferment which is capable of smoothly oxidising sugars to citric acid. The *Bacillus Acidi Lactici* is used in practice in the preparation of lactic acid. The hydrogen ions of the lactic acid produced, on reaching a concentration of about 1 per cent, act as anti-catalytes, so that, when manufacturing the acid, calcium carbonate is added, by which means the whole of the sugar is transformed into lactic acid. The active organisms in the manufacture of acetic acid (*Bacterium Aceti*) and in fermentation in tanning and similar processes, have been carefully studied, and the results have led to certain technical improvements. The bacteria of the root

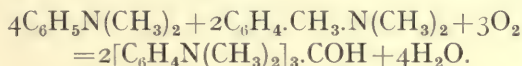
nodules of leguminous plants are cultivated industrially and supplied to farmers as "nitragin," which favours the assimilation of atmospheric nitrogen. The part played by pepsin and trypsin in digestive fermentation is of less industrial importance, though this will not be the case when we are enabled by their aid to split up proteins outside the organism to such an extent that true peptones can be supplied to the sick and feeble in a really palatable form. According to Connstein, Hoyer, and Wartenberg, the ferment contained in castor-oil seeds breaks up fats (glycerine esters of oleic, palmitic, and stearic acids) into fatty acids and glycerol. This process might play a considerable part in very different branches of chemical industry, since on the one hand the glycerol is more easily obtained than from the lyes of ordinary soap-boiling (cf. cap. VII, 5), and on the other hand the free fatty acids can be transformed into their alkali salts (soaps) using only alkali carbonates instead of hydroxides; the consumption of alkalis would be restricted, and that of the carbonates would be increased, which would give rise to a contest between the electrolytic process and the ammonia-soda process. While this is a case of replacing one of the oldest purely chemical processes by one in which the ferments formed by organisms are employed, the usual course of technical development is the reverse, the replacement of organic by more vigorous inorganic catalytes. Thus the catalytic action of hydrogen ions is used in the decomposition of fats for candle-making. This decomposition also takes place by water alone, at a high temperature; but this temperature can be considerably lowered, with corresponding economy of fuel, by adding a small quantity of calcium ions insufficient to form a lime soap, or of hydrogen ions in the form of sulphuric acid. Benzene-sulphonic acid is another catalyte which is used technically in this reaction. A small quantity of free acid is also required in the decomposition of fats by ferments. The saccharification of starch, which has been already mentioned, can also be effected by dilute sulphuric acid. In this way starch sugar is obtained, which is itself of industrial importance, but can also be used for the manufacture of pure dextrose. Hydrochloric acid is used in the manufacture of starch syrup from starch, and nitric or hydrochloric acid in that of dextrine. The catalytic acceleration of the hydrolysis of cane sugar is important industrially as leading to invert sugar, which is used as a per-

missible addition in the manufacture of wine. But on the other hand the inversion of cane sugar by hydrogen ions may prove undesirable, and in obtaining cane sugar care must be taken that it is not inverted by the carbonic or sulphurous acid used for saturation. The catalytic action of OH ions is employed in the manufacture of browning. According to P. Rohland\* OH ions retard the velocity of oxidation of iron, and this is the cause of the stability of iron in ferroconcrete, which yields OH ions by hydrolytic production of lime.

### 7. Catalytic Action in other Important Technical Processes of Oxidation, Reduction, Substitution and Condensation.

Copper compounds, like platinum compounds, serve as oxygen carriers in the preparation of formaldehyde from methyl alcohol.

Formation of methyl violet from dimethyl-aniline and dimethyl-toluidine with access of air occurs at 60° :—



Cuprous chloride acts here (perhaps also the phenol which is used as well) as oxygen carrier for the free atmospheric oxygen ; copper sulphate acts as carrier for the oxygen of potassium chlorate when this is used as an oxidiser instead of atmospheric oxygen. When copper dissolves fairly rapidly in dilute sulphuric acid, as in the preparation of copper sulphate from black copper, or when copper easily yields copper sulphate with sulphur dioxide and oxygen, as in the absorption of waste gases from the parting of gold, the carrying of oxygen by copper salts plays an important part. In the Russell process metallic silver is brought into solution by a solution of sodium copper thiosulphate. Here again, as Bodländer remarks, the catalytic action of the copper oxide separated on access of air appears to play a part in the acceleration of the process, in addition to the increase in the free energy of the process due to copper being more easily displaced by silver than hydrogen. We have already seen that ferric oxide, especially in the active form produced by the decomposition of ferric sulphate, has been proposed as a catalyte in the contact process. The catalytic action of ferric oxide appears also to accelerate the oxidation of the residual sulphur in roasting

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\* *Z. f. Elektroch.*, 15, 865.



pyrites. Iron appears to exert an influence in the roasting of zinc blende, since in the presence of much iron more sulphate is produced, though this is a point which calls for further research. It is easy to follow the cycle of intermediate reactions in the removal of sulphur compounds from illuminating gas when oxygen or air is added to the gas before purification; in this case the ferric oxide in the purifying mass is the catalyte. Again, ferric oxide carries the active oxygen of the saltpetre used to purify caustic soda from sulphides and thiosulphates. Ferric oxide is also a catalyte for atmospheric oxygen in the oxidation of naphthalene to phthalic acid and benzoic acid in presence of alkalis at  $200^{\circ}$ . It was accidentally discovered that mercury acts as a carrier in the oxidation of naphthalene to phthalic acid by the oxygen of sulphuric acid, in the same manner as it carries the oxygen of the concentrated sulphuric acid in the Kjeldahl process for the determination of nitrogen in organic substances, the acid itself yielding sulphur dioxide. Phthalic acid is the starting-point in the preparation of artificial indigo, and this convenient method for obtaining it from the cheap naphthalene first rendered possible the victory of artificial over natural indigo. Vanadium compounds should be mentioned as technically important catalytes, which have also been proposed as oxygen carriers in the contact process for sulphuric acid. In the preparation of aniline black, the oxygen of the chromic acid is carried to the aniline by vanadious chloride as well as by copper compounds. In the manufacture of fuchsine the earlier method of oxidising the mixture of aniline and toluidine with arsenic acid has been mostly replaced by oxidation with nitrobenzene, so that fuchsine is now arsenic-free. Ferric chloride is preferably used as carrier for the oxygen of the nitrobenzene, though ammonium vanadate can also be used.

### Reductions.

Organic substances can be reduced purely chemically by using different metals and different solvents; different actions are obtained according as to whether sodium, sodium amalgam, aluminium amalgam, zinc, tin, or iron are used. In those cases in which reduction is effected not by the metal itself, but by the hydrogen displaced, we can speak of catalysis in two senses:—

(a) Hydrogen is separated on different metals at different



rates. When it is rapidly evolved it has a smaller reducing power than when it is slowly evolved and possesses a higher energy-content in consequence of its higher concentration. Since this difference in the reducing hydrogen is dependent on the different catalytic activity of the metal, this is a case of catalysis.

(b) But even when we have to deal with molecular hydrogen, and the energy-content is the same, the velocity of reduction is different, as Sabatier has shown, according as to whether platinum, copper, or nickel is used as a carrier; without any catalyte the velocity is much too low. The direct reduction of nitrobenzene by the free hydrogen of water gas has been proposed technically, using copper as a carrier. Oleic acid and its glyceride, tri-olein, are transformed into stearic acid and its glyceride, tri-stearin, by free hydrogen in presence of nickel. If this process proves technically feasible in the long run, a waste product obtained in large quantities in stearin manufacture can be usefully employed.\* Nickel and iron act as catalytes in the reduction to carbon and carbon dioxide of carbon monoxide, which, as we have seen (p. 36), is unstable at rather low temperatures. In furnace working, as in the Siemens-Martin process, when the heating gas is pre-heated in heat accumulators, this effect frequently causes trouble on account of the finely divided carbon which separates. Among non-metallic reducers phosphorus is much used: as is well known, iodine is used as a carrier in this case.

### Substitutions.

Catalytes are employed in substitution processes of technical importance. In many cases the replacement of hydrogen by a halogen takes place with the velocity of an ionic reaction, but in other cases it has to be accelerated by carriers, such as iodine in chlorination reactions. Metallic chlorides, such as antimony chloride, are also much used as chlorine carriers. Aluminium chloride (also ferric or other chlorides) is used in the Friedel-Crafft reaction for the substitution of hydrogen by alkyls. Hydrochloric, or sulphuric, acid can be considered as a catalyte in the preparation of dimethyl-aniline from methyl alcohol and aniline, though it acts as a condensing agent to a comparatively very small extent as well; this applies to the hydrochloric acid

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\* [A most interesting lawsuit upon Normann's patent 1515 of 1903, dealing with this question, is going on while this book is in the press.—*Tr.*]

or zinc chloride in the formation of Malachite green from dimethylaniline and benzaldehyde with exit of water. Small quantities of benzoic or acetic acid exert a purely catalytic action in the preparation of aniline blue, when three hydrogen atoms of the rosaniline are replaced by the phenyl groups of the aniline with exit of ammonia.

We may mention finally the elimination of the diazo group by Sandmeyer's reaction, using the catalytic action of cuprous chloride and hydrochloric acid, or by Gattermann's method, using copper and hydrochloric acid. This is of technical interest, because in preparing diazo dyes copper vessels have to be avoided, in order to prevent the Gattermann-Sandmeyer reaction from taking place.

### 8. Pseudo-catalysis. The Drying of Linseed Oil.\*

The drying of linseed oil is a technical example of pseudo-catalysis, essentially consisting in an absorption of oxygen which can be accelerated by the so-called siccatives, such as the oxides of manganese, lead, and zinc. Time measurements of the oxygen absorption showed that the connection between time and amount transformed could be represented by an S-shaped curve, which is typical of auto-catalytic processes. The catalyte formed by the reaction itself accelerates the reaction-velocity to an increasing extent till finally towards the end of the reaction the moment of

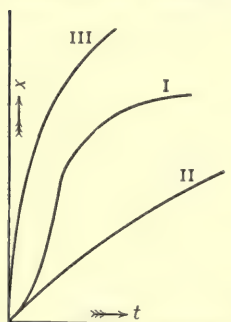


FIG. 8.

slackening comes, due to the continually decreasing concentration of the reacting substance; this causes the S-shaped course

of the  $\frac{dx}{dt}$  curve † (I, Figure 8), whereas in

normal mono- or bi-molecular reactions  $\frac{dx}{dt}$

steadily decreases (curve II, Figure 8). The curve takes the same course as II, only more rapidly, when the auto-catalyte is present at the beginning of the reaction in such an

excess, that the amount formed during the reaction can be

\* A. Genthe, *Zeits. f. angew. Chemie*, 1906, **19**, 2087.

†  $\frac{dx}{dt}$  being given by the slope of the curve at any point  $x$ .

neglected (curve III, Figure 8). Naturally there can be all possible intermediate types of  $\frac{dx}{dt}$  curve between curves II and III. The  $\frac{dx}{dt}$  curve will exhibit a more or less marked S-shape according to the smaller or larger initial concentration of the auto-catalyte. Calling  $a$  the initial concentration of the substance to be oxidised,  $x$  the amount oxidised by time  $t$ , and  $m$  the concentration of the auto-catalyte present at time 0, we have for the reaction-velocity

$$\frac{dx}{dt} = k(m+x)(a-x).$$

In fact in some experiments Genthe did observe a satisfactory constancy of  $k$ . However, even though the same sample of linseed oil was used, very different values had to be inserted for  $a$  and  $m$ ; according to Genthe this is due to a reaction which occurs together with the main reaction; this side-reaction, favoured by light and higher temperatures, and dependent on the oxygen concentration, is a combustion of the organic substance, which is generally slow. An acceleration of the drying process takes place by the addition of siccatives, such as manganese and lead compounds, to linseed oil; yet the S-shape of the  $\frac{dx}{dt}$  curve is still maintained. From what has been said above, the S-shape would have disappeared if these siccatives acted primarily on the oxidation process. A small acceleration was also observed by acids (H ions) and alkalis (OH ions), yet the S-shape of the curve was not affected. Thus Genthe assumed that the auto-catalyte has a peroxide-like character, and he confirmed this assumption by adding to the linseed oil typical peroxides such as benzene superoxide and ethyl peroxide (in the form of oxidised ether), when a very strong accelerating action was produced. Yet here again the S-shaped form of the curve was maintained. Experiments with turpentine oil have been of decisive importance. Engler and Weissberg closely studied its peroxide action and proved that a transference of active oxygen to other substances can occur by simple mixture. Old turpentine oil naturally contains more peroxide than when freshly distilled. Now Genthe found that old turpentine oil did, in fact, exert an extraordinarily high acceleration of the drying, while fresh turpentine oil was almost without



any influence. At the same time the S-shape of the curve was maintained ; this was due to the insufficient concentration of the catalyte contained in the turpentine oil, since only 5 per cent of old turpentine oil had been added. However, the expected shape of the curve was obtained by using in the experiments a mixture of fresh linseed oil with oxidised linseed oil, which thus already contained a considerable quantity of auto-catalyte. Genthe found that within the limits investigated the reaction was independent of the oxygen concentration ; this behaviour has often been observed in peroxide formation, and it supports the assumption that the auto-catalytes in drying are peroxide-like compounds. This assumption of peroxide formation is further supported by Genthe's observation of the enormous acceleration of the drying process by light, which greatly accelerates all autooxidation processes. It is mainly the rays of short wave-length which appear to be those of special activity, in agreement with the experience of painters that green, blue, and specially white colours are good driers, while red, brown, and specially black are bad driers. Oxidised turpentine oil preserves its peroxide action and only loses it on rather long heating at rather high temperatures. Linseed oil behaves similarly. Genthe found the so-called blown varnishes, e.g. linseed oil which has previously formed peroxide, are even superior in drying power to linseed oil treated with siccatives, owing to the sufficient quantity of the catalyte present. Linseed oil assumes a varnish-like character at room temperature after a sufficiently long time, while oil which has been heated too strongly ("dead-boiled" varnish) loses its drying power owing to the destruction of the catalyte. The observed acceleration of the drying process by acids is in favour of the assumption that the auto-catalyte of linseed oil is to be considered as a peroxide. Fahrion\* leaves it an open question whether the reaction is to be considered hemi-molecular, according to Engler and Weissberg, or molecular. On the former assumption siccatives would be considered as autoxidisers. However, since, according to the experiments mentioned earlier, siccatives must be considered as pseudo-catalytes, which accelerate the production of the peroxide-like auto-catalytes exerting a primary effect, we must assume the autoxy-catalysis to be molecular. There is an organic analogy for

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\* *Chemiker Zeit.*, 1903, 27, 1196.



the pseudo-catalytic action of siccatives, such as manganese and lead compounds ; this is rhusollin oleate, a manganiferous ferment occurring in the Japanese Lac tree (*Rhus vernicifera*). Its accelerating action on drying is very intense, about equal to that of light. It acts as a pseudo-catalyte, since the S-shape of the  $\frac{dx}{dt}$  curve is maintained.

### 9. Velocity of Crystallisation. Vitrification and Devitrification.

A distinction, which the present author believes to be unnecessary, is frequently drawn between catalytic phenomena and the action of crystal nuclei in bringing about the crystallisation of supersaturated solutions\* and supercooled liquids.† The action of the crystal nucleus is also catalytic (determined by its surface action), since we are dealing with the acceleration of a process which occurs spontaneously. By the action of the nuclei the active surface steadily increases during crystallisation, so that to a certain extent we are dealing with a special case of auto-catalysis, though a proportionality with the active surface of the solid crystal cannot be traced. This is confirmed by the fact, among others, that crystals below a definite size—according to Ostwald, below  $10^{-10}$  to  $10^{-12}$  grms.—do not possess the power of inducing crystallisation, i.e. with too small a surface of the inducing crystal, the initial acceleration of the crystallisation process is too small to bring about any noticeable effect in a reasonable time. The phenomena of the crystallisation of such unstable solutions or liquids are technically important in connection with devitrification, which has been studied by Guertler,‡ and Tammann.§ Tammann distinguishes between the liquid, solid crystalline, and also amorphous states of aggregation, but it appears to the present author to be difficult to fix any marked boundary between a supercooled liquid and an amorphous substance. The difference in viscosity is decisive ; but since this property always changes with temperature we will adopt the

\* Solutions containing more dissolved salt than corresponds to the solubility at a given temperature.

† Substances which are in the liquid state below the equilibrium-temperature of solid and liquid. Supercooled liquids and supersaturated solutions are thus unstable systems.

‡ *Zeit. f. anorg. Chemie*, **40**, 268.

§ *Z. f. Elektroch.*, 1904, 532.

proposal of Ostwald and consider such amorphous substances, like glass, as liquids of high viscosity. Some molten substances, especially when rapidly cooled, can be obtained in the form of such isotropic vitreous bodies. We will now consider how the spontaneous crystallisation of supercooled liquids takes place, and what are the conditions to be fulfilled, to transform a substance into this vitreous amorphous state. The spontaneous crystallisation of a supercooled liquid depends on two factors :—

- (a) On the spontaneous power of crystallisation. This is determined, and can be measured, by the number of centres of crystallisation which are formed per unit of time in unit mass of the liquid.
- (b) On the velocity with which the boundary between liquid and crystal is shifted.

Tammann comes to the conclusion that, even on highly supercooling, crystallisation never takes place homogeneously throughout the whole mass of the liquid, but only at certain points, the centres of crystallisation. Crystal threads, often arranged radially, grow outwards from these centres and, when continued, a sphere, a segment of a sphere, a spherical crystal results. In some substances the number of these spherical crystals, each of which contains a centre of crystallisation, can be readily determined by counting. For this purpose the substance is enclosed in a thin-walled glass tube, warmed above, and then rapidly cooled 40 to 80° below, the melting-point. After some time the spherical crystals formed can be counted. If this takes too long, the tube is warmed to a temperature at which the number of centres is very small, but the velocity of crystallisation is so great that the counting is ended after a few minutes. With greater supercooling the number of centres per time and temperature unit first increases, but then, at temperatures 100° below the melting-point, again decreases rapidly. The number of centres in  $\frac{1}{8}$  c.c. Betol (M.P. 95°), forming within two minutes at various temperatures, is shown graphically in Figure 9. The number of centres of crystallisation is a measure of the stability of the supercooled liquid. The more there are, the greater is the tendency of the liquid to change its state of aggregation. As the supercooling increases, the stability of the liquid first decreases, but then rises considerably as supercooling goes on.

To determine the velocity of crystallisation, the molten liquid is supercooled in a U-tube and inoculated at one end with a crystal

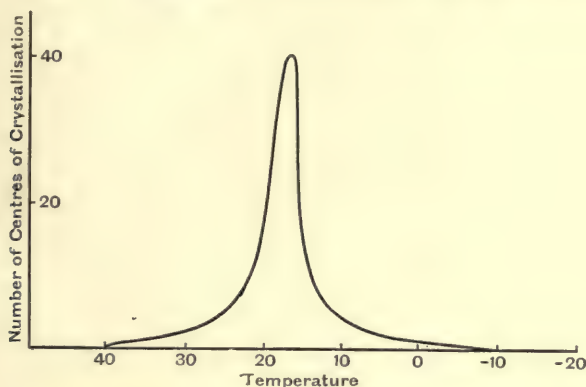


FIG. 9.

nucleus. As time goes on the crystal surface can be distinctly seen growing. Figure 10 is obtained by plotting crystallisation-velocity  $V$  against temperature. At first, in the range A, when supercooling is slight,  $V$  is small. It increases in the range B,

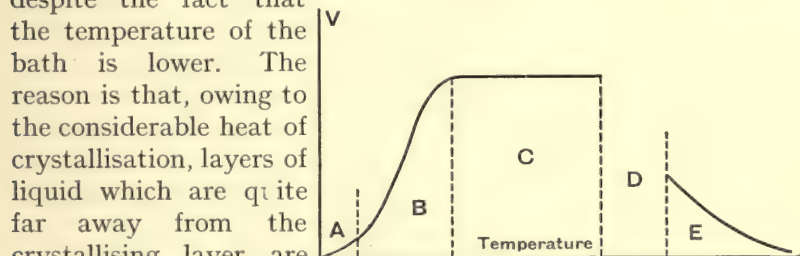


FIG. 10.

despite the fact that the temperature of the bath is lower. The reason is that, owing to the considerable heat of crystallisation, layers of liquid which are quite far away from the crystallising layer are heated to the temperature of the melting-point. Within the range A the penetration of the crystal nuclei into the layers which are too warm, owing to the insufficiently rapid removal of heat, is retarded. But  $V$  also increases when, as is the case in the range B, the removal of heat increases with falling temperature. On further decrease of temperature in the range C just so much crystallises at the visible boundary, that owing to the heat of crystallisation the temperature of melting is just established in a thin layer. In accordance with this the velocity of crystallisation is independent of the temperature. Finally at lower temperatures,

when the whole quantity present in a cross-sectional element crystallises out, the heat of crystallisation is no longer sufficient to raise the temperature of the boundary layer to the melting-point. Corresponding to this fall of temperature at the crystallisation boundary,  $V$  diminishes with increasing supercooling until it finally reaches quite a small value. Thus by sufficiently rapid cooling the crystallisation of a supercooled liquid can be brought to a standstill. If the maximum  $V$  is less than 3 mm. per minute, the heat liberated per unit of time is usually not sufficient to keep the temperature at the crystallisation boundary constant at the melting-point over a range of temperature. The consequence is that the range C (Figure 10) shrinks to a point. Substances showing a rather high velocity of crystallisation further exhibit a special temperature range D, which is lacking in substances for which  $V$  is smaller.

In this temperature range stationary velocities corresponding to the temperature of the bath cannot be realised under the ordinary conditions of conduction of heat; the heat liberated at the crystallisation boundary is here too large for the bath temperature to be steadily maintained at the boundary under given conditions of conduction of heat. Consequently from certain values of  $V$  onwards there is observed a sudden rise to its maximum value. In the range D the process of crystallisation can proceed with continual acceleration until it even becomes of an explosive character. If a supercooled liquid in the U-tube is slowly brought to a higher temperature  $V$  first increases slowly as the bath temperature rises ( $a_1$ ,  $a_2$  in Figure 11).

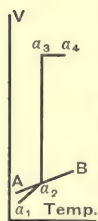


FIG. 11.

$V$  thus attains a value at which the heat liberated is too great to allow of a stationary value of  $V$ , so that  $V$  is accelerated and in a few seconds rises to the constant maximum value ( $a_2$ ,  $a_3$ ). Below AB all velocities are stationary, and above AB not stationary up to the maximum ( $a_3$ ,  $a_4$ ). These phenomena are important for the

#### Devitrification

of vitreous amorphous substances. If the temperature of such a substance is increased, devitrification will begin when the temperature range has been reached in which crystallisation centres are formed. It may happen that crystallisation centres of different polymorphic types of crystals are formed; both



types of crystals can coexist after devitrification, though only one type may remain. In devitrification, owing to the heat of crystallisation liberated, the temperature of the mass will vary according to whether the maximum  $V$  of the type which forms spontaneously is small or great. The rise in temperature  $\Delta t$  occurring at the greatest  $V$  during devitrification is determined by the value of the heat of crystallisation  $r$  and the specific heat  $c_p$  of the crystals which form :—

$$\Delta t = \frac{r}{c_p}$$

Thus, for example, if the heat of crystallisation is 50 Cal. per gram. and the specific heat of the crystals is 0.25 Cal. per gram., the temperature may rise by 200° during devitrification, if  $V$  is high. If the temperature at the beginning of the formation of crystallisation centres is 500° it would then rise during devitrification to 700° and the substance would therefore begin to glow. This phenomenon can be easily observed with  $\text{Na}_2\text{SiO}_3$ . When soda is melted with  $\text{SiO}_2$  (less than 2 grms.) and heated to 500°, a few crystallisation centres are formed, and as  $V$  is considerable, the glass soon glows. The diagram in Figure 12 shows the relation between rise in temperature and time. The branch of the curve  $a, b, c$  shows the rise in temperature due to the addition of heat from outside. If no devitrification took place the temperature of the glass would not rise above 500° or 550°. However, when spontaneous crystallisation begins, a sudden rise in temperature takes place along the branch of the curve  $c, e, f$ . If during devitrification the melting-point is reached, the temperature then remains constant for a long time until the mass is all crystallised. In the case of sodium metasilicate the melting-point (1055°) is not attained and a decrease again takes place from  $e$ . Here the heat of crystallisation per gram. at 20° is 29 Cal. The specific heat is 0.197 between 20° and 100°. This gives a calculated rise in temperature of 149°, while at 520° the observed value is 160°. The structure of the devitrified mass is determined by

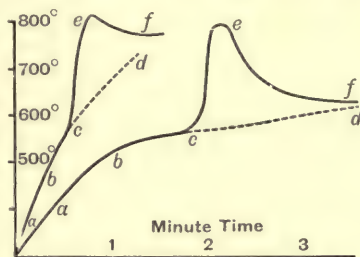


FIG. 12.

the number of crystallisation centres and the value of the maximum  $V$ .

Let us now consider the relation between spontaneous crystallisation power  $S$ , the velocity of crystallisation  $V$ , and the viscosity  $\eta$ . The viscosity of the liquid increases with the supercooling and frequently in a small range of temperature passes through all values from those of a syrupy liquid to those of a solid mass which is not deformed by the action of small forces. When the temperature is further lowered the mass becomes hard and brittle; this solidification occurs about  $90^\circ$  below the melting-point. The interdependence of the three properties  $S$ ,  $V$ , and  $\eta$

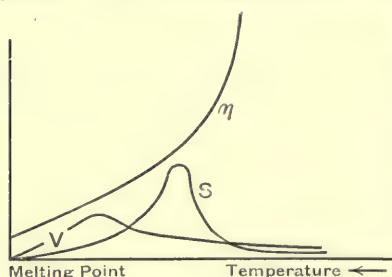


FIG. 13.

can be seen from Figure 13.

We see that after rapidly cooling past the temperature range in which numerous crystallisation centres are formed, the viscosity is very high. No crystallisation centres are then formed in the brittle vitreous mass. If these have formed during the supercooling they

will still not grow in this temperature range owing to the extraordinarily slow velocity of crystallisation. Thus within this temperature range the substance is highly stable. If the viscosity is very high even at the melting-point, as is the case in many silicates rich in alumina, the maximum values of the spontaneous crystallisation power and the crystallisation velocity are small. The shape of the viscosity curve and its relative position to the spontaneous crystallisation power curve determines whether a substance can be drawn out into thin threads or blown into vessels in the same way as glass. For a substance to be worked like glass it is a necessary condition that the number of crystallisation centres must be very small in the temperature range in which the viscosity possesses the value best suited for working the viscous liquid. It is also important that the viscosity curve should not rise too steeply, since otherwise the temperature range, in which the liquid has the most suitable viscosity, is too small, which naturally renders working very difficult. If  $a$  in Figure 14 is the range of viscosity suitable for working, then there is a bigger range of

temperatures suitable for working in curve 1 (range *b*), where the viscosity decreases slowly with temperature, than in curve 2 (range *c*), where the viscosity rapidly decreases with temperature. For many purposes it is important to be able to control the number of crystallisation centres forming in a supercooled melt. If this can be done we can obtain any substance as a crystal conglomerate or in the amorphous state, as may be desired. Explosive antimony is the only one of the metals which has been obtained in this state. A magnetic

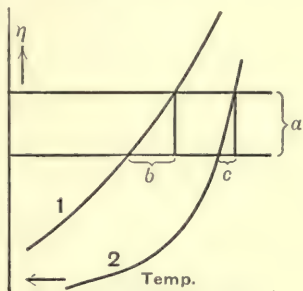


FIG. 14.

or electric field or radium radiation have no influence here, but a great effect is produced by substances dissolved in the melt. Some of these added substances depress the number of crystallisation centres to zero even in the temperature range of the maximum. Others highly increase the number without changing the temperature of the maximum. Finally some exert practically no action in small quantities. Indifferent, i.e. insoluble, substances may exert no action or an increasing or diminishing action; platinum nearly always increases the action.

We may consider substances accelerating the formation of crystallisation centres as positive, and those retarding as negative, catalytes for the process of crystallisation, in the sense that such formation is still ultimately a question of reaction-velocity. We may consider in this way the content of calcium and aluminium silicates in glass, which according to Schott favour devitrification with separation of calcium and aluminium silicate. We will return later (caps. V, 5, and V, 1) to the very similar catalytic influence of certain substances in the transformation of solid unstable to solid stable phases, e.g. the catalytic action of different metals on the changes of state in cast-iron and the mode of action of different substances in processes of hardening.

## CHAPTER III

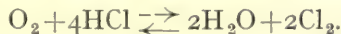
### OTHER SPECIAL APPLICATIONS OF THE LAW OF MASS ACTION— THE INFLUENCE OF TEMPERATURE ON THE EQUILIBRIUM- CONSTANT

#### 1. The Deacon Process.\*

WE have already mentioned incidentally (p. 43) that a temperature optimum must be sought in the Deacon process for chlorine. We will consider the theory of this process in some detail, choosing the experiments of Lunge as a basis. Lunge and Marmier passed dry mixtures of HCl and O or air over fragments of tiles which had been soaked in cupric chloride, dried and heated to temperatures of about  $450^{\circ}$ ; after the experiment the amount of HCl which had been decomposed was determined. Let  $x$  be the fraction of each mole HCl which is decomposed, giving  $\frac{x}{2}$  moles chlorine, and leaving  $(1-x)$  moles HCl undecomposed. The degree of decomposition is

$$\frac{\text{Cl}_2}{\text{HCl}} = \frac{x}{2(1-x)}.$$

This quotient represents the ratio of moles chlorine to moles hydrochloric acid, as well as the ratio of the volume percentages or of the partial pressures, which are proportional to the concentration. The equation of the Deacon process is



The equilibrium-constant of this process is

$$\frac{P^2_{\text{H}_2\text{O}} \cdot P^2_{\text{Cl}_2}}{P_{\text{O}_2} \cdot P^4_{\text{HCl}}} = \text{const.}$$

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\* F. Haber, *Thermodynamics of Technical Gas Reactions*, p. 180.



or

$$\frac{p_{\text{H}_2\text{O}}^{\frac{1}{2}} \cdot p_{\text{Cl}_2}^{\frac{1}{2}}}{p_{\text{O}_2}^{\frac{1}{2}} \cdot p_{\text{HCl}}} = K_p^*$$

To introduce into this expression the degree of decomposition (the ratio  $\frac{\text{Cl}_2}{\text{HCl}}$ ) we multiply numerator and denominator by  $p_{\text{Cl}_2}^{\frac{1}{2}}$  and obtain

$$\frac{p_{\text{Cl}_2}}{p_{\text{HCl}}} \cdot \frac{1}{p_{\text{O}_2}^{\frac{1}{2}}} \cdot \frac{p_{\text{H}_2\text{O}}^{\frac{1}{2}}}{p_{\text{Cl}_2}^{\frac{1}{2}}} = K_p,$$

or, introducing the value found above for the first quotient,

$$\frac{x}{2(1-x)} \cdot \frac{1}{p_{\text{O}_2}^{\frac{1}{2}}} \cdot \sqrt{\frac{p_{\text{H}_2\text{O}}}{p_{\text{Cl}_2}}} = K_p.$$

The magnitudes inside the root symbol may be partial pressures, volume percentages or moles per unit of volume, since the unit of measurement cancels out. The expression is simpler when the initial mixture is dry. In this case as much chlorine as steam is produced, so that the expression  $\sqrt{\frac{p_{\text{H}_2\text{O}}}{p_{\text{Cl}_2}}}$  has the value 1. In this case, therefore,

$$\frac{x}{2(1-x)} \cdot \frac{1}{p_{\text{O}_2}^{\frac{1}{2}}} = K_p.$$

The Deacon chlorine process obviously runs best technically when it produces much chlorine. The above formula tells us that this is the case when  $x$  is large, and  $x$  is large when at a given temperature  $K_p$  the equilibrium-constant is large. It may be concluded from the equation of equilibrium that a high excess of oxygen is favourable to decompose a high fraction of the hydrochloric acid present. In fact this is the case, but it is of little importance. As far as equilibrium is attained, the degree of decomposition is comparatively little influenced by excess

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\*  $K_p$  is the equilibrium-constant at constant pressure.

of oxygen in the gas. For the partial pressure of the oxygen does not appear itself in the equations, but only its 4th root. If the partial pressure is 0.9 atmo. in one case, and only 0.05 atmo. in another, the 4th root is 0.974 in the first case and 0.474 in the second. Thus changing the oxygen pressure by 18 times only about doubles the quotient. The degree of decomposition, which was about 0.6 before, is now 0.75, i.e. it has risen from 60 to 75 per cent.

Lunge gives the composition of the initial mixture and its pressure, from which data the partial pressure of the oxygen in the final state can be calculated. Thus Lunge and Marmier found at 430°:—

Initial gas: 8.5 % HCl, 91.5 % O<sub>2</sub> at 737 mm. pressure.

Found  $x=0.83$ .

This gives for the HCl transformed:  $0.83 \times 8.5 = 7.05$  cc., so that 3.52 cc. Cl<sub>2</sub>, 3.52 cc. H<sub>2</sub>O result.

1.76 cc. O<sub>2</sub> are consumed.

Thus the final gas has the composition (in cc.):—

| Total | Cl <sub>2</sub> | HCl  | O <sub>2</sub> | H <sub>2</sub> O | Pressure<br>in mm. |
|-------|-----------------|------|----------------|------------------|--------------------|
| 98.23 | 3.52            | 1.45 | 89.74          | 3.52             | 737                |

Accordingly,

$$p_{O_2} = \frac{89.74 \cdot 737}{98.23 \cdot 760} = 0.888 \text{ atmo.}$$

$$\therefore p_{O_2}^{\frac{1}{4}} = 0.968$$

$$\frac{x}{2(1-x)} = 2.44$$

$$\therefore \frac{x}{2(1-x)} \cdot \frac{1}{p_{O_2}^{\frac{1}{4}}} = K_p = 2.51.$$

Similar experiments by Lunge at 480° give, with a similar calculation,

| Pressure<br>in mm. | Initial gas<br>HCl % | O <sub>2</sub> % | $x$  | $p_{O_2}^{\frac{1}{4}}$ | $\frac{x}{2(1-x)}$ | $K_p$ |
|--------------------|----------------------|------------------|------|-------------------------|--------------------|-------|
| 723                | 42.2                 | 57.8             | 0.77 | 0.85                    | 1.67               | 2.0   |

From what has been said as to the free energy of the Deacon process (p. 43), we shall have at 480°

$$4.58 \log. \frac{P^2_{H_2O} \cdot P^2_{Cl_2}}{P_{O_2} \cdot P^4_{HCl}} = \frac{27,300}{753} - 3.7 \times 2.3 \log. 753 \\ + 0.0033 \times 753 - 9.92,$$

which gives 1.73 as the value of  $K_p$ .

As we see, the agreement is quite good. We see from these experiments that the position of the equilibrium is more favourable for preparing chlorine when working at lower temperatures, as we have already emphasised. Since in the Deacon process it is desired to oxidise the hydrochloric acid as far as possible to chlorine, the temperature is brought down as far as possible, but a limit is soon set by the reaction-velocity, which becomes too small in spite of the use of catalytes. Lunge and Marmier found it possible to detect quite a considerable reaction even at  $310^\circ$ , but practice has shown that the temperature must be raised above  $400^\circ$  to obtain useful results. In practice the common action of catalyte and temperature must be such that as the gas flows over the catalyte the technically important equilibrium is always produced. Lunge and Marmier took gas mixtures in which the oxygen varied from about the theoretical quantity to almost hundredfold excess. In the mixtures which only contained a little HCl, the transformation of a comparatively small quantity was enough for equilibrium to be attained. The smaller the excess of oxygen the greater must be the amount transformed, for equilibrium to be attained. Now all the gas mixtures flow over the catalyte with approximately the same velocity. The obvious result is that at rather low temperatures the gas is further from equilibrium the closer its composition approximates to that of the theoretical mixture. This can be recognised by an abnormally high retrogression of the degree of decomposition with decreasing excess of oxygen. At higher temperatures, over  $480^\circ$ , this phenomenon does not take place so markedly, from which we may conclude that at this temperature the reaction-velocity is high enough to transform even the theoretical gas mixture as far as equilibrium, therefore to the greatest possible extent.

The following table gives the experiments of Lunge at  $430^\circ$  with dry initial gas :—

| Pressure<br>in mm. | % HCl | % O <sub>2</sub> | % N <sub>2</sub> | $x$  | $p^{\frac{1}{2}}_{O_2}$ | $\frac{x}{2(1-x)}$ | $K_p$ |
|--------------------|-------|------------------|------------------|------|-------------------------|--------------------|-------|
| 737                | 8.5   | 91.6             | —                | 0.83 | 0.97                    | 2.44               | 2.51  |
| 737                | 21.0  | 79.0             | —                | 0.82 | 0.93                    | 2.28               | 2.45  |
| 729                | 34.1  | 65.9             | —                | 0.81 | 0.88                    | 2.13               | 2.42  |
| 735                | 51.1  | 48.9             | —                | 0.77 | 0.81                    | 1.68               | 2.07  |
| 729                | 67.4  | 32.6             | —                | 0.58 | 0.71                    | 0.71               | 1.00  |
| 725                | 83.1  | 16.9             | —                | 0.39 | 0.55                    | 0.32               | 0.58  |
| 726                | 6.6   | 19.5             | 73.9             | 0.79 | 0.65                    | 1.38               | 2.88  |
| 725                | 23.3  | 16.0             | 60.7             | 0.74 | 0.58                    | 1.42               | 2.45  |
| 727                | 26.0  | 15.4             | 58.6             | 0.71 | 0.57                    | 1.22               | 2.14  |
| 725                | 35.1  | 13.6             | 51.3             | 0.65 | 0.53                    | 0.93               | 1.75  |

We may conclude from this table that, when using oxygen, equilibrium occurs at an HCl content of 35 per cent. If the oxygen is partially replaced by nitrogen by using air instead of oxygen the equilibrium is not quite attained even at 26 per cent HCl, and at 35.1 per cent HCl the transformation is distinctly far from equilibrium. This shows the favourable influence of an excess of oxygen on the reaction. Lunge and Marmier expressed their surprise that in mixtures rich in hydrochloric acid, showing an equal ratio  $\frac{HCl}{O_2}$ , the degree of decomposition is higher when using mixtures of air and hydrochloric acid, than with mixtures of hydrochloric acid and oxygen; such mixtures are for example :—

| HCl  | O <sub>2</sub> | N <sub>2</sub> | $\frac{HCl}{O_2}$ | $\alpha$ |
|------|----------------|----------------|-------------------|----------|
| 72.5 | 27.5           | —              | $\frac{4}{1.51}$  | 0.50     |
| 35.1 | 13.6           | 51.3           | $\frac{4}{1.55}$  | 0.65     |

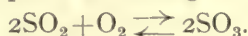
We can readily see the cause of this phenomenon. The air mixture comes fairly near to equilibrium on account of its low acid content, while in the oxygen mixture the reaction velocity is not high enough to effect the considerable change



necessary, in spite of the accelerating influence of the oxygen. A very similar application of the law of mass action can be made to the contact process for sulphuric acid.

## 2. The Contact Process for Sulphuric Acid.\*

This reaction takes place according to the equation



The equilibrium-constant is

$$\frac{p_{\text{SO}_3}}{p_{\text{SO}_2}^2 p_{\text{O}_2}^{1/2}} = K_p.$$

The quotient  $p_{\text{SO}_3} \div p_{\text{SO}_2}$  is independent of the pressure, since the unit of measurement cancels from numerator and denominator; thus the ratio of the volume percentages or concentrations can be used. In what follows we will leave out the unit of measurement in this quotient.

The process is carried out in practice to give the highest possible yield of  $\text{SO}_3$ . From the equation

$$\frac{\text{SO}_3}{\text{SO}_2} = K_p \sqrt{p_{\text{O}_2}}$$

we see that the yield of  $\text{SO}_3$  at a given temperature will be more complete the greater the partial pressure of the oxygen in the final gas; the constant  $K_p$  is greater the lower the temperature.

At a very high temperature the formation of sulphur trioxide is always considerably limited by its high dissociation into sulphurous acid and oxygen, as is found by experience. The experiments of Bodenstein gave the following values for  $K_p$  at different

temperatures  $t$ :—

| $t^\circ$ | $K_p$  |
|-----------|--------|
| 450 ..... | 187.7† |
| 500 ..... | 72.30† |
| 528 ..... | 31.3   |
| 627 ..... | 5.5    |
| 727 ..... | 1.8    |
| 897 ..... | 0.86   |

\* F. Haber, *Thermodynamics of Technical Gas Reactions*, p. 191.

† Knietsch.

On page 28 we deduced the equation

$$\frac{d \ln K}{dt} = -\frac{Q}{RT^2}.$$

This formula can be applied at once to gas reactions, taking  $K$  at constant volume ( $K_v$ ). The heat of reaction at constant volume only changes slowly with changing temperature, and it can be assumed without hesitation that at two temperatures  $t_1$  and  $t_2$  not too far apart it possesses the constant mean value  $Q_v$ . By integration between  $T_1$  and  $T_2$  we obtain

$$R \ln K_{v(1)} - R \ln K_{v(2)} = Q_v \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

In special cases the constant at constant volume  $K_v$  can be easily expressed in terms of the constant at constant pressure and vice versa. From the above we have

$$K_p = \frac{SO_3}{SO_2} \cdot \frac{1}{\sqrt{p_{O_2}}}$$

and

$$p_{O_2} = 0.0821 \times T \times C_{O_2},$$

where 0.0821 is the gas-constant in lit. atmo.,  $p_{O_2}$  the oxygen pressure in atmo., and  $C_{O_2}$  the oxygen concentration in moles per lit. Therefore

$$K_v = \frac{SO_3}{SO_2} \cdot \frac{1}{\sqrt{C_{O_2}}} = \frac{SO_3}{SO_2} \cdot \frac{1}{\sqrt{\frac{p_{O_2}}{0.0821 \times T}}} = K_p \cdot \sqrt{0.0821 \times T}.$$

The heat of reaction  $Q_v$  can be calculated from the value of  $K_p$  at different temperatures given by Bodenstein and others, by the aid of this equation which represents the change of  $K_v$  with temperature. It is found to be 21,700 Cal., and is very constant for different temperatures. Haber deduces from Bodenstein's experiments the following expression for practical purposes:—

$$RT \ln K_p = \frac{21700}{T} - 20.4.$$

The values of the equilibrium-constant  $K_p$  at constant

pressure, which is technically important when working at constant pressure, can be obtained for a given temperature by the above equation. Here, as in the Deacon process, technical interest is directed to the yield relative to the quantity of sulphur dioxide used. Calling this yield  $x$ , we have

$$x = \frac{SO_3}{SO_2 + SO_3},$$

where  $SO_3$  and  $SO_2$  are the volumes of these gases in the final gas. The ratio  $SO_3/SO_2$ , occurring in our formula, is obtained from the above equation by cross-multiplying, when

$$\begin{aligned} xSO_2 + xSO_3 &= SO_3 \\ \therefore (1-x)SO_3 &= xSO_2 \\ \therefore \frac{SO_3}{SO_2} &= \frac{x}{1-x}. \end{aligned}$$

We can thus write  $\frac{x}{1-x} \cdot \frac{1}{\sqrt{p_{O_2}}} = K_p$ ,

and knowing  $K_p$  we can calculate the yield. It is best to transform the equation, thus :—

$$\begin{aligned} \frac{x}{\sqrt{p_{O_2}}} &= K_p - K_p \cdot x \quad \therefore x = K_p \cdot \sqrt{p_{O_2}} - K_p \cdot x \cdot \sqrt{p_{O_2}} \\ \text{or } x(1 + K_p \cdot \sqrt{p_{O_2}}) &= K_p \cdot \sqrt{p_{O_2}} \\ \therefore x &= \frac{K_p \cdot \sqrt{p_{O_2}}}{1 + K_p \cdot \sqrt{p_{O_2}}}. \end{aligned}$$

The maximum theoretically attainable yield is 100x per cent. We see from the formula that the yield obviously depends on the magnitude  $K_p$ , which again only depends on the temperature. The above table shows that the influence of temperature is very considerable; as may be calculated from the formula,  $K_p$  varies from 198 at 430° to 0.36 at 900°. On the contrary, the dilution of the gas in general has but little influence on the yield which can be attained, since the partial pressure of the oxygen in the final gas, which alone comes into question, exerts an influence measured not by its concentration, but by the square root of its concentration.

We will now consider the yield as a function of the initial gas. For practical purposes it is desirable to employ a formula in which the oxygen and  $\text{SO}_2$  content of the initial gas take the place of the partial pressure  $p_{\text{O}_2}$  of the oxygen in the final gas.

Such an expression can be readily obtained by taking

$a = \% \text{ SO}_2 \text{ in initial gas}$

$b = \% \text{ O} \quad \text{,,} \quad \text{,,}$

$c = \% \text{ N} \quad \text{,,} \quad \text{,,}$

---


$$a + b + c = 100.$$

As before, let  $x$  be the yield, i.e. the ratio of the sulphur trioxide produced to the amount which might have been produced, then since half a mole oxygen is used per mole  $\text{SO}_2$ ,  $0.5ax$  parts  $\text{O}_2$  of the  $b$  present will be required to form  $\text{SO}_2$ . The volume thereby decreases from 100 to  $100 - 0.5ax$ . If the total pressure remains at 1 atmosphere, the partial pressure of the oxygen in the final gas is

$$p_{\text{O}_2} = \frac{b - 0.5ax}{100 - 0.5ax},$$

and we find

$$x = \frac{K_p \sqrt{p_{\text{O}_2}}}{1 + K_p \sqrt{p_{\text{O}_2}}} = \frac{K_p}{K_p + \frac{1}{\sqrt{\frac{b - 0.5ax}{100 - 0.5ax}}}}$$

This expression is somewhat inconvenient to handle, as it represents an equation of the third degree. But it is easy to draw a number of conclusions from it when we remember that at best the yield can be 1, i.e. if the transformation goes on quantitatively. On the other hand, the percentage of oxygen in the initial gas can be at most 100. The maximum value of the root is 1, but this would be an ideal case, and all values attainable in practice are naturally less than 1. The smaller the value of the root the higher the denominator of the fraction representing the yield, which therefore is not so good. The greater the value of the root the nearer the denominator approximates to the favourable value  $K_p + 1$ . Obviously the greater  $K_p$  the less it matters whether the root is not quite 1, but even



only  $\frac{1}{2}$  or  $\frac{1}{4}$ . In all cases the root approximates more closely to the most favourable value 1 the greater is  $b$ , i.e. the percentage of oxygen in the initial gas. If we start with pure oxygen together with a trace of  $\text{SO}_2$ , the value of the root is not appreciably

different from 1, and  $x$  is simply equal to  $\frac{K_p}{K_p + 1}$ . For tempera-

tures between  $450^\circ$  and  $500^\circ$  C. where the equilibrium-constant  $K_p$  is roughly 100, the yield of sulphuric acid given by this trace will be  $\frac{100}{101}$ , i.e. nearly theoretical. If the temperature is

only  $200^\circ$  higher, when the constant is about 3, the yield even in this ideal limiting case falls to  $x = \frac{3}{4} = 75$  per cent. Considering the trace of sulphur dioxide in atmospheric air instead of in pure oxygen, we have

$$\sqrt{\frac{b - 0.5ax}{100 - 0.5ax}} = \sqrt{\frac{b}{100}} = \sqrt{0.209} = 0.457,$$

and the yield now becomes

$$x = \frac{K_p}{K_p + 2.2}.$$

Between  $450^\circ$  and  $500^\circ$ , when  $K_p$  is about 100, the yield is still almost theoretical,  $\frac{100}{102.2}$ . But at  $200^\circ$  higher the small trace of

sulphur dioxide is only transformed into sulphur trioxide to the extent of  $\frac{3.0}{5.2} = 58$  per cent. As we see, the great difference due

to the nitrogen has very little effect at low temperatures, but a considerable effect at higher temperatures. Finally, for use with a technical roasting gas the following small table was calculated by Haber:—

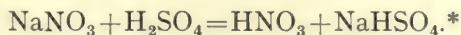
| Roasting Gas           |                       |                     | Temp.<br>in $^\circ\text{C}$ . | $K_p$ from<br>the formula | Maximum<br>yield |
|------------------------|-----------------------|---------------------|--------------------------------|---------------------------|------------------|
| $a$<br>% $\text{SO}_2$ | $b$<br>% $\text{O}_2$ | $c$<br>% $\text{N}$ |                                |                           |                  |
| 7.0                    | 10.4                  | 82.6                | 434                            | 181.0                     | 99 %             |
|                        |                       |                     | 550                            | 20.4                      | 85 %             |
|                        |                       |                     | 645                            | 5.1                       | 60 %             |

The results for high temperatures in practice sometimes exceed the calculated values when the gases have an opportunity of meeting part of the catalyte in the cooling region and thus combining further. Hence the main point is to work at quite low temperatures, i.e. to find a good catalyte which works so well that equilibrium always occurs when the gas flows over it. Platinum possesses the peculiarity, even below  $500^{\circ}$ , of accelerating sufficiently to render possible the attainment of the very favourable equilibrium possible at that temperature, and to do this with a considerable velocity of the gas. As we mentioned in the previous chapter, other catalytes are not so good. At  $850^{\circ}$  the action of fragments of porcelain is equal to that of platinum below  $500^{\circ}$ , but  $K$  is there less than 1, and thus the technical yield is very bad in this case. The ferric oxide obtained by roasting pyrites also acts as a contact substance, but its action is always smaller than that of platinum. Lunge gives the comparatively high value of 60–66 per cent for the yield obtained by using roasted pyrites, and in any case the method has the advantage of being very cheap, since the contact platinum must often be replaced, especially at first, owing to poisoning phenomena (cf. cap. II, 5).

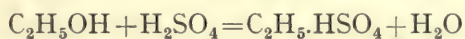
### 3. The Principle of the Displacement of Equilibrium. Manufacture of Nitric Acid and of Ether.

If we consider a reaction  $A + B \rightleftharpoons C + D$ , which leads to an equilibrium, the equilibrium equation,  $K = \frac{A \cdot B}{C \cdot D}$  (p. 14), is naturally only valid so long as all the substances participating in the equilibrium remain in one and the same phase, e.g. a gaseous or a liquid phase. If at the temperature at which the equilibrium prevails one of the substances  $C$  possesses a comparatively high vapour pressure, greater than that of the atmosphere, substance  $C$  will be continually removed from the equilibrium by boiling off. The natural result is that the equilibrium is continually displaced, and for the value of  $K$  to remain constant a fresh quantity of  $A$  and  $B$  must react, when  $C$  will be again removed by boiling off. Thus in many cases the substances  $A$  and  $B$  can be transposed into the substances  $C$  and  $D$  completely, or sufficiently so for practical purposes; the substance  $C$  which is obtained in the gaseous state can be again condensed

at another point and thus obtained. The technical manufacture of nitric acid from sodium nitrate and sulphuric acid depends on this principle :—



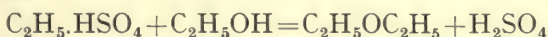
The manufacture of ethyl-ether,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ , depends on a similar displacement of equilibrium.† On heating a mixture of about one part of sulphuric acid with an excess of four parts of alcohol at the temperatures used in making ether, the equilibrium



is attained with an instantaneous velocity. The equilibrium-

constant  $\frac{C_{\text{alcohol}} \cdot C_{\text{acid}}}{C_{\text{ester}} \cdot C_{\text{water}}} = 1.7$ . Owing to the excess of alcohol

the equilibrium is considerably displaced towards the ester side. The reaction



now takes place secondarily owing to the excess of alcohol, which is still sufficient. Before the equilibrium of this second reaction has been attained the ether formed will have been removed from the reaction mixture by boiling from the first moment onwards, owing to its high vapour pressure at the temperature employed (about  $140^\circ$ ) ; it is then formed afresh, and again with the original reaction-velocity. The resulting deficiency of alcohol in the reaction mixture is rectified by allowing a mixture of alcohol and sulphuric acid to flow in. But when one charge has been worked for ether for a long time a considerable quantity of water has accumulated in the reaction mixture as the result of the first reaction, and this displaces the equilibrium away from ethyl-sulphuric acid. Finally, its concentration in the reaction mixture becomes smaller and smaller in spite of the addition of alcohol, and for this reason the reaction-velocity of the formation of ether continually decreases (cf. p. 45). Secondly, the water which is

\* With two molecules  $\text{NaNO}_3$  at higher temperatures the neutral sulphate is obtained. The heating is expensive, and, moreover, causes part of the nitric acid to decompose into oxides of nitrogen, oxygen, and water. This colours the acid red and renders condensation difficult. As well as this the retorts are badly attacked, so that the reaction is usually only carried as far as the bisulphate.

† R. Kremann, *Monats. f. Chem.*, 1910, **31**, 671.

formed retards the reaction catalytically. For both these reasons the reaction mixture is no use for making ether after some time, since the quantity of ether formed per minute is no longer large enough for the partial pressure of the ether in the vapour of the system to possess a value which will give a distillate rich enough in ether to be of practical value.

#### 4. Equilibrium in Salt Solutions. Hydrolysis and its Importance in the Manufacture of Soap.

Let us consider an aqueous salt solution. We know that all the salt is not dissolved as such, but that part of it is dissociated into ions,  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}'$ . There is an equilibrium in the aqueous solution between the ions and the undissociated salt, which is governed by the law of mass action, since the ions behave as independent substances. Writing the concentration of the undissociated salt  $C_S$  and that of the ions, of which kation

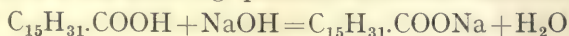
and anion result in an equivalent amount,  $C_I$ , we have  $\frac{C_I^2}{C_S} = K$ .

At a given temperature  $K$  is constant. But at any temperature there is also a definite solubility of the salt, which only depends on the undissociated part; thus, considering a salt in equilibrium with its saturated solution, we have  $C_S \cdot K = C_I^2 = \text{constant} = L$ .

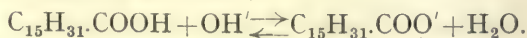
Therefore  $C_{\text{anion}} \cdot C_{\text{kation}} = \text{constant}$ . The product is termed the solubility product of the salt in question. When the ions of a given salt meet in solution and give a value  $C_{\text{anion}} \cdot C_{\text{kation}}$ , which is greater than the solubility product  $L$ , then, if equilibrium sets in, the salt in question separates out. In the reverse case solid salt is dissolved.

#### Hydrolysis.

If we add the equivalent quantity of  $\text{NaOH}$  to the aqueous solution of a weak acid, e.g. palmitic acid, the reaction



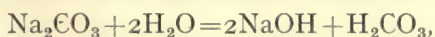
takes place, or ionically, taking the dissociation of the acid practically  $= 0$ , as a weak acid, and taking the  $\text{Na}$  salt as completely dissociated as is  $\text{NaOH}$ ,



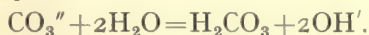


This reaction does not take place completely, but leads to an equilibrium which is governed by the equation  $\frac{\text{acid.OH}'}{\text{anion}'} = \text{constant}$ .

We arrive at the same equilibrium by dissolving the corresponding amount of the salt of the same weak acid. The practical effect of hydrolytic dissociation is that solutions of the salts of weak acids react alkaline and contain undissociated acid, e.g. sodium carbonate reacts alkaline. Moreover, this salt, of the weak carbonic acid, is appreciably hydrolytically dissociated, i.e. it reacts with the solvent water thus:—



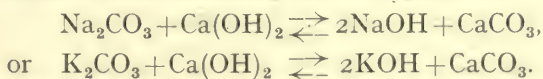
or written ionically,



We can throw back hydrolytic dissociation by highly increasing the concentration of the OH ions, i.e. by adding alkali, when the amount of undissociated acid must decrease. This is important in the manufacture of soap. If only the calculated amount of alkali is used in making soap, which consists of the Na salts of weak fatty acids, the product contains rather large amounts of the free acid. This is bad from a technical point of view, and an excess of alkali is always necessary to prevent it (cf. cap. VII, 5). A knowledge of the application of the law of mass action to electrolytic dissociation and hydrolysis is very important for the theory of the various caustification processes.

### 5. The Caustification of Sodium Carbonate by the Alkaline Earths.\*

Of late years the dye (alizarin), paper, textile, straw, and oil industries have called for more and more caustic soda. Before the electrolytic process became important, caustic alkalis were made from the comparatively easily, i.e. cheaply, prepared alkali carbonates. The method of manufacture consists in decomposing the sodium or potassium carbonate with the comparatively cheap reagent, lime, according to the equations,



\* Le Blanc and K. Novotny, *Zeitschr. f. anorg. Chem.*, 1906, **51**, 181–202, and Bodländer, *Zeitschr. f. angew. Chem.*, **18**, 1137–1141 (Lucas).

But these caustification reactions do not take place completely ; as indicated by the arrows, they are reversible. The lime reacts with the alkali carbonate, because it is more easily soluble than  $\text{CaCO}_3$ . Thus Ca goes into solution as lime and comes out as carbonate.

However, the solubility of lime and calcium carbonate is not constant, but, as can readily be seen, depends on the composition of the solution. Calcium hydroxide dissolves till its solubility-product  $K_1$  is reached, i.e. till

$$\text{Ca}^{\cdot\cdot} \times (\text{OH}')^2 = K_1.$$

If the solution already contains  $\text{OH}'$  ions, the concentration of the  $\text{Ca}^{\cdot\cdot}$  ions must be smaller for  $K_1$  to be constant, i.e. less lime dissolves in a solution of caustic than in pure water. Similarly, for calcium carbonate, the solution is saturated when

$$\text{Ca}^{\cdot\cdot} \times \text{CO}_3'' = K_2,$$

where  $K_2$  is the solubility-product of calcium carbonate in pure water. Therefore, as before, calcium carbonate is more soluble in pure water than in a solution of sodium carbonate. When lime is added to a solution of sodium or potassium carbonate, at first the lime is readily soluble and the calcium carbonate difficultly soluble, since at first there are few  $\text{OH}'$  ions and many  $\text{CO}_3''$  ions. The two solubilities become more nearly equal the further the caustification proceeds. They become equal when one substance sends as many  $\text{Ca}^{\cdot\cdot}$  ions into solution as the other, therefore when

$$\begin{aligned} \text{Ca}^{\cdot\cdot} &= \frac{K_1}{(\text{OH}')^2} = \frac{K_2}{\text{CO}_3''}, \\ \text{or } \frac{(\text{OH}')^2}{\text{CO}_3''} &= \frac{K_1}{K_2} = K. \end{aligned}$$

In other words, the caustification will stop when there is a definite ratio between the square of the concentration of the hydroxyl ions, and the concentration of the carbonate ions. The value of  $K$  is readily calculated from the solubilities of the two calcium compounds. If we assume practically complete dissociation, on account of the comparatively small solubility of the salt or the high dilution, we have for the solubility  $L_1$  of calcium hydroxide :—

$$L_1 = \text{Ca}^{\cdot\cdot} = \frac{1}{2} \text{OH}'.$$

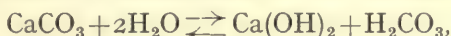
Then the solubility product  $K_1 = \text{Ca}^{++} \times (\text{OH}')^2$  and  $K_1 = L_1(2L_1)^2 = 4L_1^3$ .

But the dissociation of  $\text{Ca}(\text{OH})_2$  is not complete, being 0.80 at 0° (i.e. 0.80 moles are dissociated of every mole), according to Arrhenius.\* Therefore

$$K_1 = 4(0.80L_1)^3.$$

For calcium carbonate the solubility  $L_2 = \text{Ca}^{++} = \text{CO}_3^{--}$   $\therefore K_2 = L_2^2$ .

Here the dissociation may be taken to be complete, and there is only the hydrolytic dissociation of the calcium carbonate,



to be considered. But in this connection we can see that in the presence of many  $\text{OH}'$  ions, as in the caustification process, the hydrolysis will be thrown far back. The solubility of  $\text{CaCO}_3$  in pure water is, at 18°, 0.0128 grm. per lit., and, at 95–100°, 0.0207 grm. per lit. (Le Blanc and Novotny).† In solutions of 0.001 N.  $\text{NaOH}$ , i.e. of such a concentration that the hydrolysis is already practically completely thrown back (cf. p. 90), the solubility of unhydrolysed  $\text{CaCO}_3$  is:—

0.0035 (mean) at 18°; 0.0057 (mean) at 95–100°.

Knowing the solubility of  $\text{CaO}$  (taking this instead of  $\text{Ca}(\text{OH})_2$ ) at 18° to be 1.19 grm. per lit., we can calculate the constant  $K$  of the caustification equilibrium at 18° as follows:—

$$K_{18^\circ} = \frac{4\left(0.8\frac{1.19}{56}\right)^3}{\left(\frac{0.0035}{100}\right)^2} = 16,040,$$

in each case dividing the solubilities expressed in grms. by the molecular weight.

By neglecting the hydrolysis of the  $\text{CaCO}_3$  we obtain a value which is considerably different:—

$$K_{18^\circ} = \frac{4\left(0.80\frac{1.19}{56}\right)^3}{\left(\frac{0.0128}{100}\right)^2} = 1200.$$

\* *Zeitschr. f. phys. Chem.*, 1887, **1**, 631.

† *Zeitschr. f. anorg. Chem.*, 1906, **51**, 181.

The experiments of Le Blanc and Novotny on the equilibrium of the caustification of 1, 2, and 3 N. soda and potash solutions by means of lime at room temperature and at 100° gave the following results; the equilibrium was approached from both sides by starting with  $\text{Na}_2\text{CO}_3$  solutions, and causticising with lime, and then by starting with  $\text{NaOH}$  and decausticising with  $\text{CaCO}_3$  :—

| Starting with                 | Temp. in °C. | $\frac{C_{\text{NaOH}}}{\text{or } C_{\text{KOH}}}$ | $\frac{C_{\text{Na}_2\text{CO}_3}}{\text{or } C_{\text{K}_2\text{CO}_3}}$ | $\frac{C^2_{\text{NaOH}}}{C_{\text{Na}_2\text{CO}_3}}$ | $\frac{C^2_{\text{Or KOH}}}{C_{\text{K}_2\text{CO}_3}}$ | Yield % |
|-------------------------------|--------------|---|---|--|---|---------|
| N. $\text{Na}_2\text{CO}_3$   | room temp.   | 0.9849  | 0.0061  | 159  | —   | 98.8    |
| N. $\text{NaOH}$              | „ „          | 1.0476  | 0.0065  | 169  | —   | 98.8    |
| N. $\text{Na}_2\text{CO}_3$   | 100          | 0.9974  | 0.0047  | 212  | —   | 99.1    |
| N. $\text{NaOH}$              | 100          | 1.0174  | 0.0019  | 545  | —   | 99.6    |
| 2 N. $\text{Na}_2\text{CO}_3$ | 100          | 2.0063  | 0.0224  | 180  | —   | 97.8    |
| 2 N. $\text{NaOH}$            | 100          | 1.9373  | 0.0284  | 132  | —   | 97.2    |
| 2 N. $\text{Na}_2\text{CO}_3$ | 150          | 2.0150  | 0.0286  | 142  | —   | 97.2    |
| 2 N. $\text{NaOH}$            | 150          | 1.9240  | 0.0252  | 147  | —   | 97.5    |
| 3 N. $\text{Na}_2\text{CO}_3$ | 150          | 2.8934  | 0.1056  | 79   | —   | 93.2    |
| 3 N. $\text{NaOH}$            | 150          | 2.8047  | 0.0999  | 79   | —   | 93.4    |
| 2 N. $\text{K}_2\text{CO}_3$  | 100          | 1.8952  | 0.0252  | —  | 143   | 97.4    |
| 2 N. $\text{KOH}$             | 100          | 2.0235  | 0.0280  | —  | 146   | 97.3    |

The yield is given by the ratio  $\frac{\text{OH}}{\text{total alkali}}$  and expressed as a percentage. We see from the equilibrium equation for caustification  $K = \frac{(\text{OH}')^2}{\text{CO}_3''}$  that with increasing concentration the equilibrium must be shifted away from the  $\text{OH}'$  side, since the equation contains the square of the  $\text{OH}'$  concentration, and therefore, as the concentration rises, the  $\text{CO}_3''$  concentration does not increase directly proportional to the  $\text{OH}'$  concentration, but to its square. This theoretical conclusion is confirmed by the numbers given in the table, which show that the yields become worse as the concentration increases. The values there given show that change of temperature causes no perceptible difference in yield. Since, therefore,  $K$  only varies slightly with temperature, we can conclude from the formula given on page 28 that the heat of reaction of the process is almost zero. To



obtain a good caustification yield it is therefore necessary to work in the dilutest possible solutions, which has been also discovered purely empirically in practice. There is naturally a technical limit to this, owing to the cost of evaporating alkali solutions when too dilute. However, the experiments of Le Blanc and Novotny show the uselessness of proposals to increase the temperature and pressure as in Parnell's patents.\* A better yield can never be obtained in this way in the concentrated solutions, which are better technically for secondary reasons. A better yield in concentrated solutions can only be attained by using for the caustification the hydroxides of those alkaline earth metals in which the ratio of the solubility products of carbonate to hydroxide is greater than in the case of calcium. Magnesium is excluded, since its carbonate is more readily soluble than calcium carbonate and magnesium hydroxide, though more difficultly soluble than  $\text{Ca}(\text{OH})_2$ . Thus the equilibrium-constant would be still smaller.

The conditions are reversed for strontium and barium, since both their carbonates are more difficultly soluble than  $\text{CaCO}_3$ . The conditions are specially favourable in the case of strontium carbonate, since the experiments of Bodländer, Libau, and Lucas† show that its solubility is extremely small, and, on the other hand, the solubility of the hydroxide is not high enough for appreciable amounts to remain in solution. Lucas gives

$$K_1 = \text{Sr}^{\cdot\cdot} \times (\text{OH}')^2 = 3.73 \times 10^{-4}$$

$$K_2 = \text{Sr}^{\cdot\cdot} \times \text{CO}_3'' = 1.92 \times 10^{-9},$$

so that  $K = \frac{(\text{OH}')^2}{\text{CO}_3''} = 195,000$ , which is much greater than for calcium. In fact, the experiments of these authors show that even in concentrated solutions (3 to 4 N.) the yield is over 99 per cent. But while the heat of reaction is practically zero in the caustification by calcium hydroxide, an appreciable positive heat of reaction can be observed in caustification by strontium hydroxide. Thus it follows from the formula on page 28 that the equilibrium-constant  $K$  decreases with rising temperature, and therefore in caustification by strontium hydroxide rise in temperature is

\* Eng. Pat. 4144 of 1877 and 2203 of 1878; Ger. Pat. 3580.

† *Zeitschr. f. anorg. Chem.*, 1905, **18**, 1137.

bad for the yield. Thus caustification with strontium hydroxide is the best in practice, specially since its regeneration can easily be effected.

### 6. The Loss in the Caustification of Soda.\*

It has long been known in practice that losses of soluble caustic take place in caustification, owing to the caustic going into the  $\text{CaCO}_3$  precipitate. Wright† ascribed this to the formation of a double compound, calcium-sodium carbonate, and Scheurer-Kestner‡ to a double compound of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$ . To study these conditions more closely we must apply the phase rule, which we will consider in the next chapter. For the present purpose we may mention, however, that according to the phase rule complete equilibrium subsists when  $n$  components are present in  $n+1$  phases. Therefore in the present case, where there are four components,  $\text{CaO}$ ,  $\text{CO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{H}_2\text{O}$ , in five phases,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ , double salt, solution, and vapour, provided that pressure and temperature are fixed, the double salt in question will be in equilibrium with only one concentration of soda. The position would be otherwise if, as is improbable, there is not a new compound, but a solid solution. In this case we should have one solid phase less, and therefore incomplete equilibrium. According to the experiments of Walter,§ at  $40^\circ$  and higher temperatures a double salt, Pirssonite,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ , takes part in the equilibrium. In very concentrated soda solutions it is transformed into  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ . Walter finds for the equilibrium between  $\text{CaCO}_3$ , Pirssonite, and soda solution:—

|                                |            |            |            |
|--------------------------------|------------|------------|------------|
| Temp. ....                     | $40^\circ$ | $60^\circ$ | $80^\circ$ |
| Normality of soda solution ... | 2·14       | 3·77       | 4·34       |

At temperatures below  $40^\circ$ , Gaylussite,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ , takes part in the equilibrium, and Walter found that at  $11^\circ$  a 0·86 N. soda solution was in equilibrium with  $\text{CaCO}_3$  and Gaylussite. If we introduce in the caustification constant

\* Wegscheider, *Lieben-Festschrift*, 1906, 219.

† *Jahresber. für Chemie*, 1876, 1906.

‡ *Chem. Ber.*, 1872, 5, 983.

§ Cf. Wegscheider, *Lieben-Festschrift*, p. 219, and *Monatshefte f. Chemie*, 1907, 28, 243, 543, 555, 633.

$K = \frac{(\text{OH}')^2}{\text{CO}_3}$  the total concentrations of the alkali salts,  $\text{NaOH} = a$ , and  $\text{Na}_2\text{CO}_3 = b$ , we have

$$K = \frac{(\text{NaOH})^2}{\text{Na}_2\text{CO}_3} = \frac{a^2}{b}$$

In consequence of the change in the degree of dissociation and hydrolysis the above equation for  $K$  will not hold on dilution, but within a considerable range of concentration the ratio  $\frac{a^2}{b}$  can be considered a linear function of the total titre  $\tau = a + b$ . Expressing  $\tau$ ,  $a$ , and  $b$  in normalities (gram. equiv. per lit.), we have at  $80^\circ$ , when  $\tau = 2.0$  to  $3.9$ ,  $\frac{a^2}{b} = 133.74 - 26.55\tau$ , and when  $\tau = 4.9$  to  $5.6$ ,  $\frac{a^2}{b} = 47.16 - 5.537\tau$ .

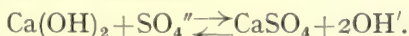
The curves of these two equations intersect at  $\tau = 4.083$ . At  $108^\circ$ , for example, in the range of concentration from  $\tau = 4.4$  to  $4.7$ , there is such a change in the course of the ratio  $\frac{a^2}{b}$ . The point at which the isotherm bends, though its position does not appear to be established quite definitely, means a change in the nature of the solid phase. Thus we may say that at a low concentration  $\text{CaCO}_3$ , and at higher concentrations, a calcium-sodium carbonate (but at  $80^\circ$  Pirssonite) is the solid phase. From what has been said already, we see that both solid phases can only coexist in equilibrium under quite definite conditions of temperature and concentration, i.e. at the point of intersection of the two isotherms. Thus from the experiments of Walter and Wegscheider we see that in technical caustification the formation of a double salt can occur in different ways. The equilibria determined by Walter relate to the stable form of  $\text{CaCO}_3$ , and provided that this results, double salt formation may occur during caustification itself; the temperature employed, at which the reaction-velocity is suitable for technical working, is about  $108^\circ$ , and at this point double salt is formed when the concentration of the solution is high (about  $4.4$  to  $4.7$  N.). The temperature falls on decantation and filtration, and we have already seen that at lower temperatures Pirssonite may be formed at lower concentrations. In fact it is formed at  $80^\circ$  in



solutions slightly over 4 N., and at 40° in solutions only 2.5 N. The velocity of formation of Pirssonite is quite high enough, at all events at 80°, for it to be formed to a considerable extent. The concentration may be still further lowered by contamination of the lye with other sodium salts. The experiments of Walter and Wegscheider show also that there is the possibility of double salt formation at still lower concentrations in presence of excess of  $\text{Ca}(\text{OH})_2$ , since the  $\text{Ca}(\text{OH})_2$  may first give a labile form of  $\text{CaCO}_3$ , or perhaps the velocity of formation of Pirssonite may be higher than that of  $\text{CaCO}_3$ . Thus the formation of double salt is conceivable at 108° in less than 4.4 to 4.7 N. solutions. It is true that Pirssonite again decomposes to form a stable form of  $\text{CaCO}_3$ , but experience shows that this decomposition is incomplete, perhaps owing to the formation of a layer of  $\text{CaCO}_3$  protecting the Pirssonite particles and preventing equilibrium from being attained. The experiments show that these double salts, which are undesirable in practice, are only capable of existence above a certain carbonate concentration, from which it is obvious that once they are formed, they can be decomposed again by pure water. Thus it should be possible to remove the caustic from the carbonate precipitate obtained in caustification by sufficient, repeated stirring and washing. In fact Smith and Liddle\* have found that the precipitate can be completely freed from caustic by boiling with water. Yet in technical caustification there are losses of caustic up to 2 per cent, which shows that it is not profitable to carry out the thorough washing necessary owing to the retardation, in the transformation of the Pirssonite, by a protective layer of  $\text{CaCO}_3$ . Essentially similar considerations apply to the losses in washing out crude soda in the Le Blanc process.

### 7. The Caustification of Potassium Sulphate.†

There is a distinct technical importance in processes by which caustic is prepared from the cheap alkali sulphates instead of from the comparatively dear carbonates. The process of Clausen‡ was based on the reaction



\* *Chem. News*, 1881, 43, 9.

† J. Herold, *Z. f. Elektroch.*, 1905, 11, 417.

‡ Eng. Pat. 13956 of 1852.



## THE CAUSTIFICATION OF POTASSIUM SULPHATE 97

The transposition resembles the carbonate caustification in being incomplete, but it stops sooner at an equilibrium. Taking the concentration of the two calcium salts as constant, since they are present as solid phases, we have as the condition of equilibrium the simple expression

$$\frac{(\text{OH}')^2}{\text{SO}_4''} = K.$$

Let us first assume, as we did for the carbonate caustification, that the dissociation of both calcium salts is complete, and we can then calculate the value of  $K$  in the same way as before, except that we have  $L_{\text{CaSO}_4}$ , instead of  $L_{\text{CaCO}_3}$ :

Thus 
$$K = \frac{4L^3 \text{Ca}(\text{OH})_2}{L^2 \text{CaSO}_4}.$$

Herold gives the following values for the solubility of  $\text{CaO}$ , gypsum, and anhydrite: the values of  $K$  given in the last column are calculated neglecting the dissociation:—

| Temp. °C. | Solubility in grms. per lit. |                                      |                   | K      |
|-----------|------------------------------|--------------------------------------|-------------------|--------|
|           | CaO                          | CaSO <sub>4</sub> ·2H <sub>2</sub> O | CaSO <sub>4</sub> |        |
| 0         | 1·31                         | 1·759                                | —                 | 0·3064 |
| 20        | 1·17                         | 2·036                                | —                 | 0·1640 |
| 70        | 0·75                         | 1·890                                | —                 | 0·0496 |
| 150       | 0·17                         | —                                    | 0·528             | 0·0060 |
| 190       | 0·084                        | —                                    | 0·031             | 0·0006 |

Taking into consideration the dissociation of  $\text{Ca}(\text{OH})_2$ , which at 0° is 0·8,\* and that of gypsum, which at 0° is 0·6,† we have

$$K = \frac{4\left(0\cdot8 \times \frac{1\cdot31}{56}\right)^3}{\left(0\cdot6 \times \frac{1\cdot759}{136}\right)^2} = 0\cdot4366.$$

The small value of the constant shows that the yield in this process is essentially smaller than in the caustification of sodium carbonate: this must be balanced against the much greater cheapness of the process. Herold investigated the equilibria by

\* See p. 91.

† Boyer and Hullet, *Zeit. f. phys. Chem.*, **37**, 385, and **42**, 577. Van 't Hoff, **45**, 257.

starting with 0.1 to 1.5 N.  $K_2SO_4$  solutions, causticising with lime, and 0.1 to 1.5 N. KOH solutions, decausticising with  $CaSO_4$ . Results obtained for the ratio of  $OH'$  to  $SO_4''$ , at temperatures from 0° to 190°, are given in the following table:—

| Initial solution                           | Temp °C. | Millimoles<br>OH | Millimoles<br>$SO_4$ | K     |
|--|----------|------------------|----------------------|-------|
| 0.1 N. $K_2SO_4$                           | 190      | 53               | 27                   | 0.106 |
| 0.5 N. $K_2SO_4$                           | 190      | 90               | 180                  | 0.045 |
| 1.0 N. $K_2SO_4$                           | 190      | 94               | 249                  | 0.034 |
| 0.5 N. KOH                                 | 190      | 92               | 160                  | 0.053 |
| 0.1 N. $K_2SO_4$                           | 150      | 41               | 38                   | 0.044 |
| 0.5 N. $K_2SO_4$                           | 150      | 82               | 190                  | 0.036 |
| 1.5 N. $K_2SO_4$                           | 150      | 92               | 320                  | 0.032 |
| 0.5 N. KOH                                 | 150      | 91               | 200                  | 0.042 |
| 0.1 N. $K_2SO_4$                           | 70       | 40               | 32                   | 0.050 |
| 0.5 N. $K_2SO_4$                           | 70       | 70               | 215                  | 0.022 |
| 1.0 N. $K_2SO_4$                           | 70       | 100              | 264                  | —     |
| 2.0 N. $K_2SO_4$                           | 70       | 210              | 464                  | —     |
| 0.5 N. KOH                                 | 70       | 80               | 210                  | 0.034 |
| 0.1 N. $K_2SO_4$                           | 20       | 60               | 35                   | 0.105 |
| 0.5 N. $K_2SO_4$                           | 20       | 103              | 101                  | 0.102 |
| 1.0 N. $K_2SO_4$                           | 20       | 198              | 248                  | —     |
| 1.5 N. $K_2SO_4$                           | 20       | 269              | 318                  | —     |
| 0.1 N. $K_2SO_4$                           | 0        | 64               | 36                   | 0.112 |
| 0.5 N. $K_2SO_4$                           | 0        | 123              | 120                  | 0.127 |
| 1.0 N. $K_2SO_4$                           | 0        | 223              | 183                  | —     |
| 1.5 N. $K_2SO_4$                           | 0        | 278              | 213                  | —     |
| Saturated with<br>$K_2SO_4$ + solid salt } | 0        | 400              | 298                  | —     |

The agreement between the values of K found experimentally at 20° is very good: at 0° and 70° there is agreement in order of magnitude, while at 150°–190° the agreement is bad. There are several reasons for this:—

(1) Herold calculates  $K = \frac{(OH')^2}{SO_4''}$  by taking the total hydroxide and sulphate concentration instead of the ionic concentration.

(2) The ratio between the degree of dissociation of potassium hydroxide ( $\alpha$ ) and of potassium sulphate ( $\beta$ ) changes with temperature. The dissociation of the sulphate rises with rising

temperature, that of the hydroxide falls. Thus at  $0^\circ$  the ratio  $\frac{\alpha^2}{\beta}$  is  $\frac{0.8}{0.6}$ , but at  $20^\circ$  and  $70^\circ$  it approximates to the value 1, so that the influence of the degree of dissociation becomes smaller. Accordingly at  $20^\circ$  and  $70^\circ$  the results deviate least from theory. However, when the temperature rises higher a deviation in the opposite direction can be observed, since the calculated are smaller than the observed values.

(3) The solubility of calcium sulphate changes as the temperature rises in a different way than would be expected from the data for lower temperatures.

Herold's results are shown graphically in Figure 15, in which the OH concentrations are ordinates and the  $\text{SO}_4$  concentrations abscissæ. The curves for  $0^\circ$ ,  $20^\circ$ , and  $70^\circ$  show distinct bends; as we have said above, at these points there is a change in the solid phase from  $\text{CaSO}_4$  to syngenite, a double salt of the composition  $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . Thus to a certain extent it

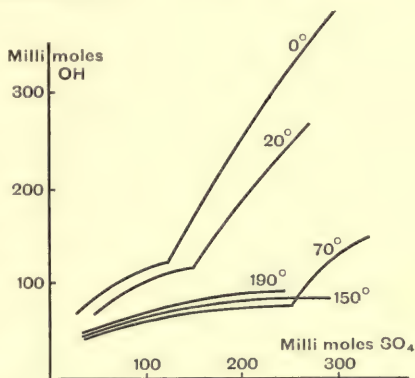
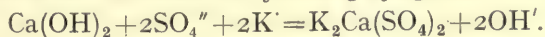


FIG. 15.

does not appear to be advisable technically to work with rather high concentrations of  $\text{K}_2\text{SO}_4$ , since losses of potassium occur. The equation for the reaction yielding syngenite is:—



The constant of this equation,  $K_1 = \frac{(\text{OH}')^2}{(\text{K}')^2 \cdot (\text{SO}_4'')^2}$ .

Starting from pure  $\text{K}_2\text{SO}_4$ , when  $\text{K}' = \text{SO}_4''$ , we have

$$K_1 = \frac{(\text{OH}')^2}{(\text{SO}_4'')^4},$$

or, changing the constant to simplify the expression,

$$K'_1 = \frac{\text{OH}'}{(\text{SO}_4'')^2}.$$

Therefore in caustification in dilute solution, when  $\text{CaSO}_4$  is the solid phase, and when  $\text{K}' = \frac{(\text{OH}')^2}{\text{SO}_4''}$ , the yield of soluble alkali

is greater the higher the dilution: when syngenite is the solid phase the reverse holds, and a better yield is obtained at higher concentrations.

It can be seen both from the calculated and observed values of  $K$  that it is smaller at higher temperatures, and it is thus best to work at the lowest possible temperature. The influence of concentration is far less than in the case of the caustification of the alkali carbonates. This is mainly due to the difference in solubility between calcium hydroxide and sulphate being less than that between hydroxide and carbonate. To take an example of the yield: at  $0^\circ$  there is equilibrium in  $0.1$  N. solution when  $0.065$  N. caustic is present, and apparently the yield is 65 per cent. However, we must remember that the solution is still  $0.034$  N. in  $\text{Ca}^{++}$ .<sup>\*</sup> Therefore this yield of 65 per cent will only be obtained by concentration of the solution separated from the solid phase, if the calcium comes down as gypsum. The yield is essentially decreased if part of the  $\text{Ca}$  separates out as hydroxide: in the limit, if it all separated out as hydroxide, the yield would be  $\frac{(0.065 - 0.034)100}{0.1} = 31$  per cent, instead of

65 per cent. In a  $0.2$  N. solution at equilibrium the  $\text{OH}'$  is  $0.095$  N. and the sulphate  $0.12$  N. It will be seen by calculating from the solubility product that this corresponds to  $0.016$  N.  $\text{Ca}^{++}$ . Assuming that on evaporation the  $\text{Ca}^{++}$  all comes out as lime, which is not far from the truth, according to Herold, the final yield will be  $\frac{(0.095 - 0.016)100}{0.2} = 39$  per cent, which is not essen-

tially different from the final yield in  $0.1$  N. solution with the same assumptions. A glance at the  $0^\circ$  isotherm of Figure 15 will show that the same yield can also be attained by keeping the solution saturated with  $\text{K}_2\text{SO}_4$  during the reaction. The number of operations is increased by one, in this case, since in concentrated solutions syngenite is formed as solid phase, and to avoid losses of  $\text{K}_2\text{SO}_4$  it must be decomposed by water. However

---

\* The solubility of calcium is about  $1.4$  at  $0^\circ$ . Assuming complete dissociation into  $\text{Ca}^{++}$  and  $2\text{OH}'$ , the solubility product is  $\left(\frac{1.4}{56}\right) \cdot \left(\frac{1.4}{28}\right)^2 = 4 \times (0.025)^3$ . In the above table at  $0^\circ$  in  $1$  N. solution there are about  $0.06$  moles  $\text{OH}'$  per lit.,  $x \times 0.06^2 = L = 4 \times 25^3 \times 10^{-9} (x = \text{Ca}^{++}) \therefore x = \frac{25^3}{9} \times 10^{-5} = 0.017$  moles per lit.





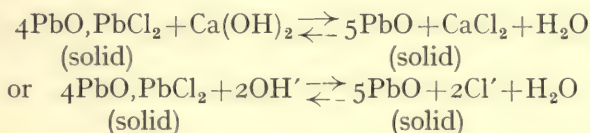
tions, since the difference in degree of dissociation between NaOH and NaCl is not so great as that between NaOH and  $\text{Na}_2\text{CO}_3$ . However, purely mechanical disturbances exert a greater influence, for while in dilute solution, especially with excess of NaCl, the litharge is satisfactorily transposed to the basic salt, this only occurs in more concentrated solutions when the litharge is particularly finely divided. When using rather large amounts of litharge in concentrated solutions it may become coated over, and this phenomenon hinders the equilibrium from being attained. As we shall see later, this is the cause of the unfavourable effect when using the high concentrations which are otherwise so desirable in practice, and on this account Berl and Austerweil have observed an optimum effect on adding a definite amount of litharge. The results obtained with such definite amounts of litharge at  $18^\circ$ ,  $48^\circ$ , and  $74^\circ$  are given in the following table :—

| Temp. $^\circ\text{C}$ . | Concentration of NaCl | Moles NaOH per lit. | $K = \frac{\text{OH}'}{\text{Cl}'}$ | Maximum yield of NaOH in per cent of amount capable of being formed |
|--------------------------|-----------------------|---------------------|-------------------------------------|---|
| 18                       | N/20                  | 0.0245              | 0.961                               | 49.0  |
| 18                       | N/10                  | 0.0501              | 1.004                               | 51.3  |
| 18                       | N/5                   | 0.115               | 1.351                               | 57.7  |
| 18                       | N/2                   | 0.240               | 0.923                               | 48.1  |
| 18                       | N/1                   | 0.465               | 0.869                               | 46.4  |
| 18                       | 2 N                   | 0.829               | 0.71                                | 41.5  |
| 18                       | 5 N                   | 1.66                | 0.50                                | 33.2  |
| 48                       | N/20                  | 0.026               | (1.090) ?                           | (52.3) ?  |
| 48                       | N/10                  | 0.038               | 0.613                               | 36.3  |
| 48                       | N/5                   | 0.077               | 0.629                               | 38.5  |
| 48                       | N/2                   | 0.213               | 0.741                               | 42.6  |
| 48                       | N/1                   | 0.404               | 0.676                               | 40.4  |
| 48                       | 2 N                   | 0.705               | —                                   | 37.5  |
| 48                       | 5 N                   | 1.690               | —                                   | 26.7  |
| 74                       | N/20                  | 0.0196              | 0.645                               | 39.2  |
| 74                       | N/10                  | 0.0380              | 0.610                               | 38.7  |
| 74                       | N/5                   | 0.074               | 0.588                               | 36.7  |
| 74                       | N/2                   | 0.183               | 0.578                               | 36.8  |
| 74                       | N/1                   | 0.327               | 0.488                               | 32.9  |
| 74                       | 2 N                   | 0.590               | —                                   | 29.4  |
| 74                       | 5 N                   | 1.284               | —                                   | 25.7  |

These experiments show that there is a fair constancy in the values of  $K$  up to about  $N/1$  solutions, and the results show that the yield is practically independent of the concentration, as required by theory. At higher concentrations equilibrium is not reached, owing to the phenomenon of coating-over, already mentioned, and the values of  $K$  are then too small. The yield is obviously greater the higher the value of  $K$ . Concerning the influence of temperature, the table shows that  $K$  steadily falls as the temperature rises. Thus in practice it is advisable to work at the lowest possible temperature. There remains to be noted the important practical point that litharge is partly dissolved by the alkaline solution; according to Berl and Austerweil it dissolves in  $N/1$   $\text{NaOH}$  as monosodium plumbite,  $\text{Pb} \begin{smallmatrix} \text{ONa} \\ \text{HO} \end{smallmatrix}$

and in more concentrated solutions as  $\text{Pb}(\text{ONa})_2$ .

The regeneration of the solid phase  $4\text{PbO}, \text{PbCl}_2$  by  $\text{Ca}(\text{OH})_2$  is of technical importance. The equilibrium-constant of the reaction



is also  $K = \frac{\text{OH}'}{\text{Cl}'}$ . Thus, in contradistinction to the main reaction,

the regeneration goes better the smaller the value of  $K$ . Berl and Austerweil found:—

| Using   | At 18°                              |                              | At 74°                              |                              |
|---|-------------------------------------|------------------------------|-------------------------------------|------------------------------|
|   | $K = \frac{\text{OH}'}{\text{Cl}'}$ | % of solid phase regenerated | $K = \frac{\text{OH}'}{\text{Cl}'}$ | % of solid phase regenerated |
| Stoichiometric amounts of lime water and $4\text{PbO}, \text{PbCl}_2$ . | 0.93                                | 51.1                         | 0.52                                | 64.8                         |
| Excess of $4\text{PbO}, \text{PbCl}_2$ .                                | 1.01                                | 24.0                         | 0.53                                | 29.9                         |
| Excess of lime water . . .  | 1.22                                | 89.2                         | 0.55                                | 87.3                         |

Since, as shown by the results, the constant falls as the temperature rises, rise in temperature is favourable for the regeneration process, as the yields in the above table show. Moreover, these numbers show that the yield is essentially increased by using more  $\text{Ca}(\text{OH})_2$ . By combining the two factors, excess of lime and increase of temperature, or by treating several times with

fresh insufficient amounts of lime water, it is thus possible to reconvert the solid phase, lead oxychloride, into litharge completely enough for practical purposes. A sample regenerated in this way was found by Berl and Austerweil to contain 98.86 % PbO and 1.03 % CaO, and to exert the same action in the main process as a sample of fresh litharge which had not been used at all.



## CHAPTER IV

### DISSOCIATION PRESSURE—APPLICATION OF THE PHASE RULE

#### 1. The Phase Rule.

WHEN water is placed in a vacuum, some of it evaporates, but usually not all. Enough evaporates to produce water vapour at a perfectly definite pressure, and there is such a definite pressure for every temperature. The temperature at which the vapour pressure reaches 760 mm. is called the boiling-point of water at atmospheric pressure.

Considering water vapour alone, or indeed any gas alone, it may have different pressures at a given temperature (Boyle's Law). A gas is therefore said to possess two degrees of freedom, and this also holds for a solid or liquid in a vessel which is quite closed.

A liquid and vapour together, or a solid, such as ice, and vapour together, have only one perfectly definite vapour pressure at a given temperature ; thus either of the factors, pressure or temperature, can be chosen arbitrarily, but the other factor is then defined. Such a system, called biphasic, has thus only one degree of freedom.

The relationship between temperature and pressure can be represented by a vapour pressure curve. Water and ice have the same vapour pressure at  $0.0077^{\circ}$ , i.e. their vapour pressure curves intersect at this point. Water vapour, liquid, and ice coexist at this point only (supercooling and similar phenomena, which mean unstable systems, are obviously excluded). Three phases of a substance or component can coexist at such a point, for water at  $0.0077^{\circ}$  and a pressure of 4.57 mm. There is no degree of freedom ; we cannot choose pressure or temperature arbitrarily, and there is only one pair of pressures and temperatures at which a given substance can simultaneously exist in three phases, solid, liquid, and gaseous. These facts can be

expressed quite generally by the phase rule, which states that the number of phases (P) minus number of components (C) equals 2 minus number of degrees of freedom (F) :—

$$P - C = 2 - F$$

or  $F = 2 - P + C.$

Considering water vapour, liquid water, or ice alone we have one substance  $H_2O$  in one phase; the number of degrees of freedom  $F = 2 - 1 + 1 = 2$ ; thus we can choose arbitrarily pressure and temperature. Such an equilibrium is termed incomplete, bivariant. The fields of three possible bivariant equilibria

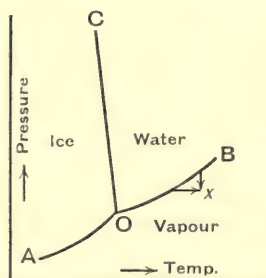


FIG. 16.

are shown in Figure 16 by the marked areas. Ice-vapour, water-vapour, water-ice, are systems with two phases of one component and there is therefore one degree of freedom. We can choose the temperature, for example, arbitrarily, but then if there is equilibrium the pressure is defined. Such an equilibrium is termed complete or univariant; it is represented by a curve, in the present case by the vapour pressure curve of ice AO, the

vapour pressure curve of water OB, and the curve OC, which represents the change in melting-point with pressure. At the point O, where there is equilibrium between the three phases of one substance, there is no longer any degree of freedom, i.e. there is only one definite temperature and pressure at which there is equilibrium between the three phases of one substance. Such an equilibrium is termed invariant; the point is termed a triple or singular point.

Let us consider now a system of two substances, e.g. a dilute solution of sulphuric acid or a saturated solution of common salt with solid salt at the bottom. Each system has a definite vapour pressure for every temperature. But the sulphuric acid changes in vapour pressure on further addition of acid, while a further addition of solid salt has no effect whatever on its saturated solution.

If the volume of the space containing sulphuric acid is enlarged, more water evaporates, the solution becomes more concentrated, and its vapour pressure lower. If this is done for the

salt solution the vapour pressure is not lowered, since salt separates out from the solution in proportion to the water which evaporates. As we see, the change in volume has the effect of transferring a substance from one phase to another. In the first example the gaseous phase is enriched in water vapour at the expense of the liquid phase: in the second example the solid phase also is enriched at the expense of the liquid phase. Therefore in the sulphuric acid solution, at a given temperature, we can obtain any number of different pressures by increasing one substance or another, in short, by changing the proportions. While various pressures are possible in the sulphuric acid solution, only one is possible in the saturated salt solution. The sulphuric acid solution is a case of incomplete, bivariant equilibrium. There are two phases, solution and vapour, and two components,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ . Applying the phase rule we find in fact that  $F = 2 - 2 + 2 = 2$ . In the saturated salt solution with solid salt at the bottom there are, however, three phases, vapour, solution, and solid salt, and two components,  $\text{H}_2\text{O}$  and  $\text{NaCl}$ . Therefore the number of degrees of freedom is one, and the equilibrium is complete, univariant.

We have already applied the phase rule (cap. III, 6) to the calcium-sodium carbonate double salts, which are important as explaining the losses in the caustification of soda. We mentioned that there is univariant equilibrium when the four components  $\text{CaO}$ ,  $\text{CO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{H}_2\text{O}$  are present in the five phases  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ , double salt, solution, and vapour, i.e. at a given temperature the occurrence of double salt as a solid phase is only possible at a given concentration of the liquid phase. We will now apply the phase rule to those systems in which one or more solid substances dissociate at a given temperature, yielding a gaseous phase, or the gaseous phase reacts with a solid body, in either case till the "dissociation pressure" corresponding to the temperature in question has been attained.

## 2. Lime-burning.

When calcium carbonate is heated it decomposes into lime and carbon dioxide. This chemical reaction, "lime-burning," is one of the oldest chemical processes, since the lime produced was used for mortar thousands of years ago. The phenomena observed on heating  $\text{CaCO}_3$  are quite similar to those on evaporat-

ing water. If  $\text{CaCO}_3$  is heated in a vacuum, e.g. at  $547^\circ$ ,  $\text{CO}_2$  and  $\text{CaO}$  are only formed till the concentration of  $\text{CO}_2$  is sufficient to give a  $\text{CO}_2$  pressure of 27 mm. Hg. The  $\text{CaCO}_3$  can again dissociate if this  $\text{CO}_2$  is pumped off, but only till the  $\text{CO}_2$  pressure again reaches 27 mm. This pressure is always reached as long as there is enough  $\text{CaCO}_3$  present to yield the necessary amount of  $\text{CO}_2$ . On the other hand, if a sufficient quantity of  $\text{CaO}$  is brought in contact with  $\text{CO}_2$  at  $547^\circ$  the gas is absorbed till its pressure is 27 mm. As in the case of water, there is a perfectly definite pressure for each temperature and vice versa.

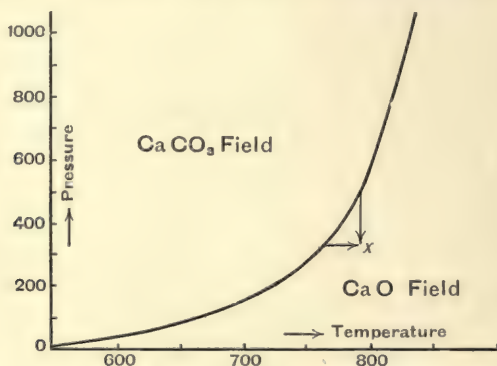


FIG. 17.

The corresponding pairs of values are as follows :—

|                   |            |
|-------------------|------------|
| $547^\circ$ ..... | 27 mm. Hg. |
| $610^\circ$ ..... | 46    ,,   |
| $625^\circ$ ..... | 56    ,,   |
| $740^\circ$ ..... | 255   ,,   |
| $745^\circ$ ..... | 289   ,,   |
| $810^\circ$ ..... | 678   ,,   |
| $812^\circ$ ..... | 763   ,,   |
| $865^\circ$ ..... | 1333   ,,  |

We can thus construct a vapour pressure curve, separating the fields of existence of  $\text{CaCO}_3$  and  $\text{CaO}$ , quite like that for the system water – water vapour. As in the latter case the pressure was independent of the amounts of water and water vapour, so also in this case the dissociation pressure is independent of the amounts of the two solid substances, calcium carbonate and

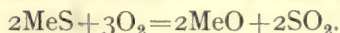


lime, and of the amounts of the solid and gaseous phases. The phase rule shows that this is correct. There are two components,\*  $\text{CaCO}_3$  and  $\text{CO}_2$ , in three phases,  $\text{CO}_2$ ,  $\text{CaO}$ , and  $\text{CaCO}_3$ . From the phase rule  $P - C = 2 - F$  we have  $F = 2 - 3 + 2 = 1$ . Thus there is one degree of freedom, i.e. there is a definite pressure at every temperature; the equilibrium is univariant or complete. The burning of lime should not be effected, therefore, under  $812^\circ$ , since it is only at this temperature that the carbon dioxide reaches atmospheric pressure, when the gas can escape sufficiently fast; however, this high temperature is too expensive. It is convenient to burn at lower temperatures and pass a current of inert gas such as air over the heated material. The inert gas acts to a certain extent like a vacuum and the  $\text{CO}_2$  pressure over the heated material corresponding to a given temperature will be a partial pressure in the whole gas, e.g. at  $625^\circ$ , a partial pressure of  $\text{CO}_2$  of 56 mm. When the  $\text{CO}_2$  corresponding to this pressure is carried off the equilibrium is disturbed and a fresh quantity of  $\text{CaCO}_3$  gives off  $\text{CO}_2$ , forming  $\text{CaO}$ ; this reaction goes on till the whole of the  $\text{CaCO}_3$  is dissociated.

### 3. Roasting Reactions in General.†

(Nordhausen sulphuric acid.)

Roasting consists of complete oxidation of metallic sulphides to oxides by atmospheric oxygen at a high temperature.

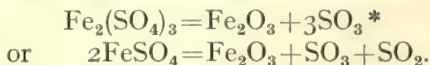


While the reverse of this reaction, the reduction of  $\text{MeO}$  by  $\text{SO}_2$ , has not yet been observed, sulphate often results instead of oxide as the product of oxidation. This is not to be wondered at, since  $\text{SO}_2$  in presence of  $\text{O}_2$  is in a state of unstable equilibrium and  $\text{SO}_3$  is formed, especially by the action of the catalytic metallic compounds as in the contact process for sulphuric acid, and if there is equilibrium the amount will depend only on the temperature. The  $\text{SO}_3$  so formed reacts with the metallic oxide to a univariant equilibrium,  $\text{MeO} + \text{SO}_3 \rightleftharpoons \text{MeSO}_4$ , which is exactly like the dissociation of calcium carbonate,  $\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$ . There is a definite pressure of  $\text{SO}_3$  corresponding to every temperature. The reverse reaction, the

\* Not three, for the amount of  $\text{CaO}$  is equivalent to the  $\text{CO}_2$  formed.

† R. Schenck, *Physikalische Chemie der Metalle*, pub. Knapp, Halle, 1909.

dissociation of metallic sulphates, is employed in making Nordhäusen sulphuric acid by heating iron sulphate.

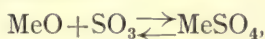


When  $\text{SO}_3$  is obtained, it is dissolved in an insufficient quantity of water to give fuming or Nordhäusen sulphuric acid. Thus the amount of sulphate formed in roasting depends on the partial pressure of the  $\text{SO}_3$ .

Now in the gas phase,  $\text{SO}_3$  is in equilibrium with  $\text{SO}_2$  and  $\text{O}_2$ , and at any temperature we have †

$$K_p = \frac{p_{\text{SO}_2}^2 \cdot p_{\text{O}_2}}{p_{\text{SO}_3}^2} \text{ or } p_{\text{SO}_3} = p_{\text{SO}_2} \sqrt{\frac{p_{\text{O}_2}}{K_p}}.$$

Taking  $p_{\text{SO}_3}$  as the dissociation pressure of sulphur trioxide in the univariant equilibrium



there is equilibrium between the solid products of roasting, oxide and sulphate, when

$$p_{\text{SO}_3} = p_{\text{SO}_2} \sqrt{\frac{p_{\text{O}_2}}{K_p}},$$

where  $p_{\text{SO}_2}$  and  $p_{\text{O}_2}$  are partial pressures of  $\text{SO}_2$  and  $\text{O}_2$  in the roasting gases.

If

$$p_{\text{SO}_3} > p_{\text{SO}_2} \sqrt{\frac{p_{\text{O}_2}}{K_p}}$$

sulphate will be formed in the roasting, but if

$$p_{\text{SO}_3} < p_{\text{SO}_2} \sqrt{\frac{p_{\text{O}_2}}{K_p}}$$

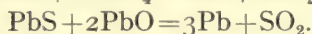
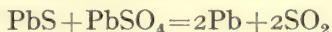
\* It appears from the recent work of Bodenstein and Tatsuji Susuki (*Z. f. Elektroch.*, 1910, **16**, 912) that  $\text{SO}_2$  and  $\text{O}_2$  are formed first,  $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1\frac{1}{2}\text{O}_2$ , and these then react secondarily,  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ . The equilibria  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  and  $3\text{SO}_3 + \text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3$  will thus result indirectly.

† Here the equilibrium-constant is the reciprocal of that previously employed, but this is of no importance in the present case.

sulphate will decompose, i.e. oxide will be formed in roasting. In some cases the roasting can be carried out to yield metal direct. This interesting reaction is employed in the metallurgy of copper and of lead.

#### 4. Lead Roasting.

In the case of lead,\* which we will now consider more fully, the reactions are usually formulated as follows :—



However, these reactions only proceed in this way under definite conditions : deviations from these are to be found in the Huntingdon-Heberlein lead-smelting process, in which the following reaction occurs :—



At rather high temperatures Jenkins and Smith † observed that sulphur dioxide is partially absorbed by lead. As Bodländer ‡ has suggested, the reactions in roasting are reversible, as in the case of lime-burning. When a comparatively large amount of CaO is brought in contact with some CO<sub>2</sub> at 625°, the whole amount of CO<sub>2</sub> is not absorbed, but enough remains to give the dissociation pressure of CO<sub>2</sub> at 625°, which is 56 mm. Thus if CaO, CaCO<sub>3</sub>, and CO<sub>2</sub> are brought together at a given temperature, the amount of CO<sub>2</sub> and therefore its partial pressure will determine in which direction the reversible reaction CaCO<sub>3</sub> → CaO + CO<sub>2</sub> will proceed. Similar conditions can be observed in roasting lead. We will employ the phase rule as a guide to the many equilibria which are possible here. There are three components, lead, sulphur, and oxygen. The solid or liquid phases capable of existence are lead, lead sulphate, lead sulphide, lead oxide, and there is also gaseous sulphur dioxide. On bringing any three phases together and heating to a given temperature we then obtain a univariant equilibrium, i.e. there will be a definite SO<sub>2</sub> pressure which only depends on the temperature. The four substances mentioned, which can occur in four separate liquid

\* Schenck and Rassbach, *Ber.*, 1907, **40**, 2185, 2950. Cf. also Schenck, *Phys. Chem. der Metalle*, loc. cit.

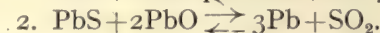
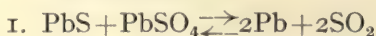
† *Jour. Chem. Soc.*, 1897, **71**, 666.

‡ *Berg-u. Hütt. Zeit.*, 1898, 409.

or solid phases, can interact with  $\text{SO}_2$ , giving four univariant equilibria :—

|       |     |                   |     |
|-------|-----|-------------------|-----|
| 1. Pb | PbS | PbSO <sub>4</sub> | —   |
| 2. Pb | PbS | —                 | PbO |
| 3. Pb | —   | PbSO <sub>4</sub> | PbO |
| 4. —  | PbS | PbSO <sub>4</sub> | PbO |

It has been shown that of these four combinations only the first two correspond to different equilibria.



When  $\text{PbSO}_4$ ,  $\text{PbS}$ , and  $\text{Pb}$  are heated,  $\text{SO}_2$  is evolved and a corresponding pressure is observed for each temperature.

600°—38.8 mm.

680°—282.3 mm.

639°—105.4 mm.

700°—442.2 mm.

723°—735.0 mm.

These equilibria can also be reached from the other side, for if  $\text{SO}_2$  is allowed to act on  $\text{Pb}$  the following pressures are observed after a fairly long action :—

635°—100.7 mm.

671°—239.9 mm.

690°—353.0 mm.

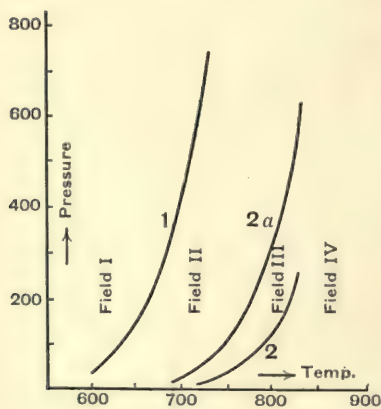


FIG. 18.

712°—14.1 mm.

827°—276 mm.

776°—59.9 mm.

847°—546 mm.

800°—92.0 mm.

870°—857 mm.

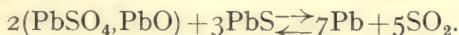
These points lie well on curve 1 in Figure 18, which corresponds to equilibrium 1. The  $\text{SO}_2$  pressure of equilibrium 2 has to be obtained by heating the mixture of  $\text{PbS}$ ,  $\text{PbO}$ , and  $\text{Pb}$ , which evolves  $\text{SO}_2$ . However, the reaction is first noticeable at 700°. The conditions here are not so simple as before. The following values (curve 2 in Figure 18) are obtained by starting with mixtures of  $\text{PbS}$  and  $\text{PbO}$ , which give off  $\text{SO}_2$  :—



Other conditions being the same, the following higher values for pressure are obtained by reaching equilibrium from the other side, by starting at higher temperatures when more  $\text{SO}_2$  has been formed and then allowing to cool, i.e. to absorb  $\text{SO}_2$  :—

|              |              |
|--------------|--------------|
| 710°—69 mm.  | 802°—435 mm. |
| 774°—268 mm. | 822°—660 mm. |
| 835°—860 mm. |              |

The reason why this new equilibrium curve is obtained is that owing to the high temperature the lead oxide is molten, and there is a certain amount of sulphate contained in it through the action of the sulphur dioxide. On cooling, instead of the pure substances, lead sulphate or lead oxide, a basic sulphate\* of the composition  $\text{PbSO}_4 \cdot \text{PbO}$  separates out. The curve *2a* in Figure 18 thus corresponds to the new equilibrium,



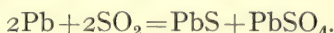
This view is shown to be correct by the fact that equilibria between sulphide, metal, and  $\text{SO}_2$  are obtained, which show the following connection between  $\text{SO}_2$  pressure and temperature, by starting with masses obtained by melting sulphate and oxide together (about 39 to 60 per cent sulphate), i.e. rich in basic sulphate  $\text{PbSO}_4 \cdot \text{PbO}$  :—

|              |              |
|--------------|--------------|
| 681°—16 mm.  | 795°—306 mm. |
| 741°—81 mm.  | 821°—548 mm. |
| 770°—184 mm. | 830°—710 mm. |

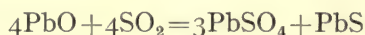
These values fall right on curve *2a*, which proves that the two equilibria are identical. The tension curves 1, *2a*, 2, in Figure 18, representing the above univariant equilibria, bound the four fields of bivariant equilibria, which are of technical interest. Let us recall the fields of existence of water and water vapour. At the point *x* in Figure 16, which we reach by starting from the curve of univariant equilibrium, and either raising the temperature or lowering the pressure, all the water turns into water vapour. In the same way all the calcium carbonate is decomposed by raising the equilibrium temperature or lowering the equilibrium pressure, say at *x* (Figure 17). In either case

\* This separates out together with pure  $\text{PbSO}_4$  at a fairly high content of  $\text{PbSO}_4$ , and with another basic sulphate,  $\text{PbSO}_4 \cdot 2\text{PbO}$ , at a low  $\text{PbSO}_4$  content (cf. cap. V, 3).

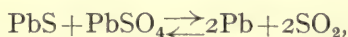
we have passed from a univariant to a bivariant equilibrium. The case of lead-smelting is very similar to this. Taking the field I of Figure 18, PbS and PbSO<sub>4</sub> are capable of existence, just as in the previous examples water or water vapour, or CaO or CaCO<sub>3</sub>, were capable of existence within a given field. The following reactions take place in field I:—



Therefore in field I sulphide and sulphate do not interact. The same end products are produced in field I by the interaction of SO<sub>2</sub> and PbO,



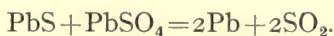
(PbO is formed by the intermediate reaction  $3\text{Pb} + \text{SO}_2 = \text{PbS} + 2\text{PbO}$ ). Curve 1, which divides fields I and II, corresponds to the equilibrium



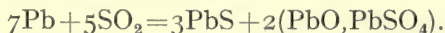
in the same way as the vapour pressure curve of water corresponds to the equilibrium,  $\text{water} \rightleftharpoons \text{water vapour}$ .

In field II PbS and the basic sulphate PbO, PbSO<sub>4</sub> are capable of existence.

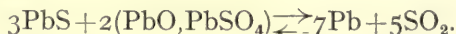
In field II the following reactions take place, giving PbS and PbO, PbSO<sub>4</sub>,



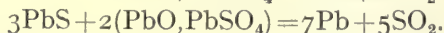
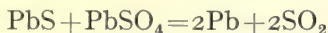
Pb is not formed as such, but reacts



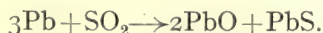
In field II the basic sulphate does not react with lead sulphide. In field III PbS and PbO are capable of existence together. The limiting curve 2a between fields II and III corresponds to the equilibrium



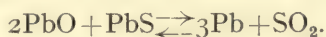
In field III, where PbS and PbO can coexist, the following reactions will take place:—



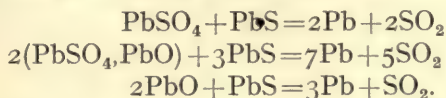
The metallic lead cannot exist in field III, but turns into PbO and PbS,



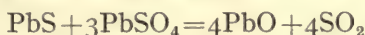
The limiting curve between fields III and IV corresponds to the equilibrium



Thus in field IV only metallic lead would be in equilibrium with  $\text{SO}_2$ . The following reactions take place :—



Briefly applying this to technical practice, we may say that if we wish to prepare metal direct without subsidiary reactions by smelting sulphate and sulphide, or oxide and sulphide, we must perform the heating within field IV. We must either employ very high temperatures or keep the pressure of the sulphur dioxide low by evacuation or by passing an inert gas. If we wish to obtain litharge by smelting, as in the Huntingdon-Heberlein process, according to the reaction



we work in field III.

Huntingdon and Heberlein mix the ore with lime and blow air through the previously heated mixture. They assume that lime here exerts a catalytic action by forming calcium superoxide as an intermediate product, which gives up its oxygen more readily. However, it is possible that the lime only lowers the temperature sufficiently to bring us from field IV into field III.

### 5. The Reactions in the Blast Furnace.\*

The production of carboniferous pig-iron in the blast furnace is of comparatively early date. Before that time tough malleable iron poor in carbon was directly prepared from iron ore and red-hot wood charcoal. This was done in small furnaces about a yard high. Increasing need for the metal led to the furnaces being made larger and being provided with a blast, since the natural draught and simple bellows were no longer sufficient to maintain the heat. The first continuously working blast furnaces appeared in the thirteenth century. They furnished an easily

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\* R. Schenck and Zimmermann, *Ber.*, 1903, **36**, 1231-1251. R. Schenck, *Z. f. Elektroch.*, 1904, **10**, 397. R. Schenck, Semiller, Falke, *Ber.*, 1907, **40**, 1704. R. Schenck, *Phys. Chem. d. Metalle*, *loc. cit.*

melting pig-iron rich in carbon, which had to be first decarburised for working into malleable iron and steel. The diagram-

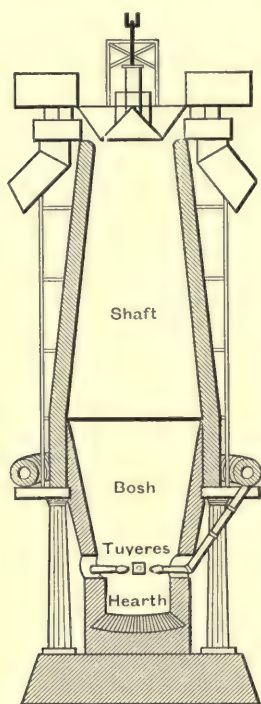


FIG. 19.

matic form of the blast furnace is extremely simple; the different parts are shown in Figure 19. The conical shaft is charged alternately with coal, ore, and slag-forming material through the throat. Below the shaft there is the funnel-shaped bosh, above the structure containing the inlets for the blast, i.e. the tuyeres, and, finally, the hearth. Let us follow the passage of the ore, consisting of oxides, through the furnace. In the uppermost zone the hot furnace gases effect drying of the material, which gradually falls into regions of continually higher temperature. We have already seen (p. 40) that the reduction of oxide to metal is effected by carbon monoxide which results in the lower zones by the action of the blast on the highly heated carbon. Owing to the pre-heating of the air the temperature of combustion is high, over  $1100^{\circ}$ , so that it will be readily understood that practically pure CO results (cf. p. 41). The following table shows the high percentage of com-

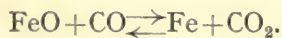
combustible substances in the waste gases of blast furnaces:—

|                    |         |
|--------------------|---------|
| $N_2$ .....        | 54—66 % |
| $CO_2$ .....       | 7—19 %  |
| CO .....           | 21—31 % |
| $H_2$ .....        | 1—6 %   |
| Hydrocarbons ..... | 0—6 %   |

These facts suggested to technologists that the waste gases could be collected and their great thermal value utilised. In the modern blast furnace the hot waste gases are led away and employed for pre-heating the blast, or they used to be employed for heating steam-boilers and for other purposes. We have already seen (p. 21) that the direct explosion in gas-engines of a mixture of air and purified waste gas gives a far greater efficiency than by the employment of steam-boilers and steam-engines.

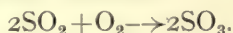


These waste gases furnish mechanical energy for steel works generally, for driving rolling-mills and dynamos, giving light and power for many industrial purposes, and in this way a rational utilisation of the by-product has been obtained which is of the utmost economic value in the steel industry. The question now arises whether it ought not to be possible to employ these gases, which are so rich in the powerfully reducing CO, for the reduction of further ore. In fact, at one time much attention was directed to this point in this country. It was considered that it ought to be possible to transform a considerable part of the carbon monoxide into dioxide by lengthening the layer of hot oxide through which the reducing oxides have to pass. For this purpose furnaces were built higher and higher till they became towers up to 33 yards high. This was expensive, and even then it was not possible appreciably to lower the carbon monoxide content of the gas. At the time this appeared very puzzling and merely had to be left as a fact. We can now explain it by the principles of heterogeneous equilibrium. Le Chatelier was the first to note that the reaction between carbon monoxide and iron oxide was reversible. On passing a stream of carbon dioxide over heated metallic iron it is found that a considerable part of the dioxide is reduced to monoxide, while the iron is oxidised. For this reason it is impossible completely to reduce carbon monoxide to dioxide. Under these conditions the oxidisability of the monoxide is limited, like the reducibility of the dioxide by metallic iron. This reversibility is expressed by the equation

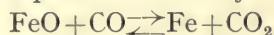


It is of interest to determine the conditions under which reduction or oxidation takes place. Baur and Glässner have recently made comprehensive experiments on this point. They treated ferrous oxide with CO and also metallic iron with CO<sub>2</sub>, in each case in a closed vessel at constant temperature. Analysis of the resulting gas showed that the composition of the gaseous mixture, the ratio monoxide to dioxide, was equal in the two cases. Thus the state of equilibrium was attained, in which neither reduction nor oxidation can occur. The equilibrium is between two solids, iron and ferrous oxide, and the gaseous mixture. There is a difference between this and the earlier processes, such as the dissociation of calcium carbonate, in that the gaseous

phase is a mixture, and the concentration of the components of this phase comes into question. The principle of Le Chatelier (cf. p. 28) states that addition of heat favours reactions which proceed with absorption of heat, e.g. the dissociation of  $\text{CaCO}_3$ , while addition of heat influences unfavourably those reactions which proceed with evolution of heat, e.g. the frequently mentioned and very important reaction



Reactions with no heat effect are not influenced. In the same way pressure favours reactions which take place with diminution of volume; on the other hand, when external pressure is reduced the opposite reaction takes place with increase of volume, as in burning lime or roasting lead. Chemical systems which react in either direction without change of volume do not change their equilibrium with pressure. The system



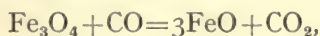
belongs to this latter class, and we can conclude from this that as far as equilibrium is concerned it is immaterial whether the gases are in presence of the solid components at many atmospheres or only a few millimetres pressure. When the temperature is constant it is only the relative volume of the gases which is of importance. There is a homogeneous equilibrium in the gas phase, and for each temperature there is a definite ratio between monoxide and dioxide in equilibrium with the solid substances. When this ratio is altered a reaction occurs reduction by increasing the monoxide, oxidation of the metal by

increasing the dioxide. This equilibrium ratio  $\frac{C_{\text{CO}}}{C_{\text{CO}_2}} = \eta$  is of

importance in the theory of the blast furnace. The following results have been obtained:—

| Temperature | CO   | CO <sub>2</sub> | $\eta$ |
|-------------|------|-----------------|--------|
| 552°        | 54   | 46              | 1·16   |
| 596°        | 56   | 44              | 1·25   |
| 651°        | 58   | 42              | 1·38   |
| 662°        | 58·4 | 41·6            | 1·404  |
| 680°        | 59   | 41              | 1·44   |
| 750°        | 61   | 39              | 1·56   |
| 850°        | 68   | 32              | 2·12   |
| 900°        | 71·5 | 28·5            | 2·51   |

This shows that the value of  $\eta$  varies with the temperature fairly considerably in an upward direction, and also that it is impossible to obtain waste gases poor in carbon monoxide. The ratio  $\text{CO}:\text{CO}_2$  is found to lie between the values 2.44 and 1.04 in practice, which agrees well with the above equilibrium values at different temperatures. The variations can thus be explained, firstly, by different temperatures in the blast furnace. Secondly, the ores consist of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , and, *a priori*, we should expect these higher oxides to give rise to other equilibria. We know that ferroso-ferric oxide can be reduced to ferrous oxide by a mixture of carbon monoxide and dioxide in equal volumes, and it is obvious that this process can come into play in the blast furnace. The reaction is

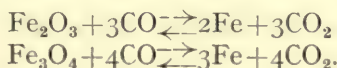


and is governed by the same law as the reduction of ferrous oxide.

The equilibrium-constant  $\eta' = \frac{\text{CO}}{\text{CO}_2}$  was determined at different temperatures by Baur and Glässner,\* whose results are given below. The values of  $\eta'$  are naturally different from those found for  $\eta$  in the reduction of ferrous oxide.

| Temperature | CO | CO <sub>2</sub> | $\eta'$ |
|-------------|----|-----------------|---------|
| 450°        | 46 | 54              | 0.812   |
| 490°        | 47 | 53              | 0.887   |
| 550°        | 44 | 56              | 0.786   |
| 650°        | 37 | 63              | 0.587   |
| 850°        | 26 | 74              | 0.351   |
| 950°        | 23 | 77              | 0.299   |

But it is not necessary for the reduction of higher oxides to take place in stages, and a direct reduction to metal is conceivable. We possess no similar data for the equilibrium of the systems



But, from the fact that the heats of reaction are extremely small, Le Chatelier has deduced that the equilibrium will only be shifted to an inconsiderable extent by the change in temperature, and will thus remain practically constant at all temperatures.

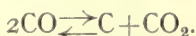
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\* *Zeitschr. f. physik. Chemie*, 1903, **43**, 361.



In making ferro-manganese and spiegeleisen (5 % C and 5 to 25 % Mn), highly manganiferous ores are employed in the blast furnace. Manganese is not so noble as iron, which is shown in practice by the state of equilibrium being comparatively higher oxidised. Thus the equilibrium gas mixture will contain more carbon monoxide than in the case of iron, and the waste gases will be especially rich in CO. Hence there is a great variety of reactions which may occur in the blast furnace, so that the composition of the waste gases is essentially dependent on the nature of the ores which are being smelted, and on the temperature of the furnace. These considerations explain why the ratio  $\text{CO}:\text{CO}_2$  is subject to such great variations under different conditions.

Simple reduction of oxides by carbon monoxide is not the only reaction taking place in the blast furnace. Sometimes there is observed the separation of large quantities of extremely finely divided carbon, which gives trouble in working, and causes the so-called hanging or scaffolding of the charge. The carbon is produced by the decomposition of carbon monoxide (cf. cap. I, 9, and p. 65).



The reaction is reversible, since carbon monoxide can be produced by passing the dioxide through red-hot carbon. This equilibrium is different from the former, since CO decomposes with diminution of volume and is formed with increase in volume. Thus from Le Chatelier's principle a gas under a high pressure will contain relatively more  $\text{CO}_2$  than a gas under a lower pressure. The conditions of equilibrium can be formulated from the law of mass action: two molecules CO and one molecule  $\text{CO}_2$  take part in the reaction, and there is equilibrium when

$$\frac{C^2_{\text{CO}}}{C_{\text{CO}_2}} = \xi,$$

where  $\xi$  is constant at a given temperature.

It is further interesting to ascertain the change of  $\xi$  with temperature. We have already seen (I, 9) that the decomposition of carbon monoxide takes place with considerable evolution of heat; therefore rise in temperature must throw back the decomposition of CO, as shown by the following results of Boudouard:—



| Temperature | CO   | CO <sub>2</sub> |
|-------------|------|-----------------|
| 450°        | 2    | 98              |
| 600°        | 23   | 77              |
| 700°        | 68   | 42              |
| 850°        | 94   | 6               |
| 1000°       | 99.3 | 0.7             |
| 1050°       | 99.6 | 0.4             |

Thus the decomposition of CO takes place especially at low temperatures.

There is a difference in the value of  $\xi$  depending on the modification of carbon which is in equilibrium with the two gases; e.g. it will be different for graphite, for the carbon deposited from CO, or for amorphous carbon (wood or sugar charcoal). Schenck and Heller found that the values of  $\xi$  for these three modifications of carbon at 600° were in the ratio 1:5:5.5. This difference is a necessary consequence of the law of mass action, since the

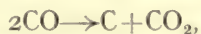
equilibrium-constant is really  $K = \frac{C^2_{CO}}{C \times C_{CO_2}}$ , where C is the vapour

pressure of carbon; however, since this is constant we write

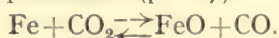
$K.C = \xi = \frac{C^2_{CO}}{C_{CO_2}}$ . But since C, the vapour pressure of carbon,

varies from one modification to another, the value of  $\xi = KC$ , though constant for any particular modification, will be different for different modifications.

The decomposition of carbon monoxide only takes place with an unmeasurable velocity even at comparatively high temperatures, and for the reaction to take place at a measurable velocity the presence of a catalyte is necessary (p. 65), such as the metals of the iron group, nickel, cobalt, iron, and manganese. The two latter metals are present in the blast furnace, so that there is sufficient opportunity for the decomposition to take place. There is a difference between the catalytic action of nickel and iron. At a certain temperature nickel only brings about the equilibrium



while iron as a baser metal is oxidised by the carbon dioxide formed, giving the equilibrium (p. 117)



By applying the phase rule to the equilibrium between iron, ferrous oxide, carbon, and its two gaseous oxides, CO and CO<sub>2</sub>, we find that as the system consists of three components (C, Fe, and O) and four phases (Fe, FeO, C, and gas), it must be a univariant equilibrium, possessing one degree of freedom, i.e. there is a definite equilibrium pressure at each temperature. This can be easily deduced from the equilibrium equations of the two systems, iron, ferrous oxide, CO, and CO<sub>2</sub>, where  $\eta = \frac{\text{CO}}{\text{CO}_2}$ , and carbon, CO, and CO<sub>2</sub>, where  $\xi = \frac{(\text{CO})^2}{\text{CO}_2}$ .

Let  $x$  be the number of CO molecules and  $1-x$  those of the dioxide; if  $P$  is the total pressure of the two gases the respective partial pressures are

$$xP \text{ and } (1-x)P.$$

These magnitudes are proportional to the concentrations of the two gases, and we can insert them into the above equilibrium-constants giving

$$\eta = \frac{x}{1-x}, \text{ and } \xi = P \cdot \frac{x^2}{1-x}.$$

Since at total equilibrium the value of  $x$  for the two partial equilibria must be equal, we can eliminate  $x$  from these equations, obtaining the expression

$$P = \xi \cdot \frac{1+\eta}{\eta^2}.$$

This confirms what we have already deduced from the phase rule, that there is a definite gas pressure  $P$  at each temperature.

From the equation  $\frac{x}{1-x} = \eta$  it follows that the composition of the gas is also definitely fixed.

The point of total equilibrium at a given temperature can be found graphically by plotting the total pressures  $P$  as ordinates and the compositions of the gas phase, the percentages of CO,  $x$  as abscissæ. Let us consider the conditions at 700°. The equilibrium between Fe, FeO, CO, and CO<sub>2</sub> at a given temperature (Figure 20) is represented by the straight line A, i.e. oxidation takes place to the left of A and reduction to the right. The curve B represents the relation between the pressure and the

temperature of carbon (produced in the amorphous form from CO) with its oxides,

$$\xi = P \cdot \frac{x^2}{1-x}$$

These curves intersect at the point of total equilibrium, the co-ordinates of this point being  $P = \xi \cdot \frac{1+\eta}{\eta^2}$ ,  $x = \frac{\eta}{1+\eta}$ . We have just observed that  $\xi$  varies with the modification of carbon used, and  $\xi'$  for graphite is less than  $\xi$  for amorphous carbon, and thus  $P = \xi' \cdot \frac{1+\eta}{\eta^2}$  will be smaller for graphite.

The curve C in Figure 20, for the graphite—CO—CO<sub>2</sub> equilibrium, is lower than that for amorphous carbon—CO—CO<sub>2</sub>, and thus it cuts the line A at a lower point.

The fields I, II, III, IV, and IV' have each a definite meaning. In fields I, IV, and IV' there is a reduction of ferrous oxide or of iron oxide in general to metallic iron. But while in field I carbon coexists with iron in stable equilibrium, in field IV graphite and amorphous carbon serve as reducing agents, forming oxides of carbon. Finally, in field IV' only amorphous carbon, but not graphite, is burnt to oxide in the reduction.

In field II carbon and metal oxide can coexist with the gaseous carbon monoxide, while in field III the metal oxide alone is in stable equilibrium and oxidation takes place by carbon passing into oxide without the metal oxide being attacked. It is important to establish the conditions under which carbon monoxide is decomposed, as in the presence of nickel, without there being an oxidation of the iron, and the conditions under which simultaneous oxidation takes place. Let us start with pure carbon monoxide and decompose it purely catalytically. Knowing the initial pressure  $P_0$ , and observing the new pressure  $P$  after a certain time, we can find how great is the partial pressure  $p$  still

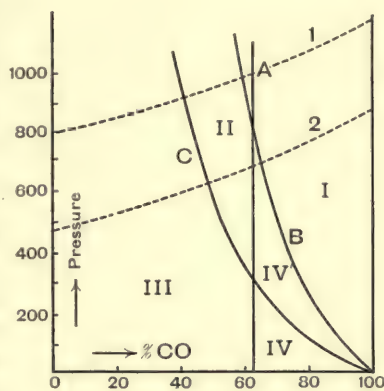


FIG. 20.

remaining ( $p$  always refers to CO). The difference  $P_o - P$  gives half the partial pressure of the monoxide already decomposed, since one volume  $\text{CO}_2$  is produced instead of two volumes CO; therefore  $p = P_o - 2(P_o - P) = 2P - P_o$ .

Since  $p = xP$ , we have  $P_o = (2 - x) \cdot P$ . This equation is that of a hyperbola, and represents the path of the reaction in the decomposition of carbon monoxide. It depends on the magnitude of the initial value  $P_o$  whether the reaction first proceeds along the curve of the equilibrium Fe, FeO (at high values of  $P_o$  Figure 20, curve 1), or the curve of the equilibrium CO,  $\text{CO}_2$  (at small values of  $P_o$ ; Figure 20, curve 2). In the limit the path of the reaction meets the point of total equilibrium. By inserting the co-ordinates of the total equilibrium (p. 123) in the equation  $P_o = (2 - x) \cdot P$  we obtain as the initial pressure of the carbon monoxide

$$P_o = \left(2 - \frac{\eta}{(1 + \eta)}\right) \cdot \xi \cdot \frac{1 + \eta}{\eta^2} = \xi \cdot \frac{2 + \eta}{\eta^2}.$$

When  $P_o$  is greater than this value (Figure 20, curve 1) the metal is oxidised until the total equilibrium is attained; when  $P_o$  is smaller (Figure 20, curve 2) the metal acts solely as a contact substance. In the case of the blast furnace it is chiefly important to know the pressure of the total equilibrium at different temperatures. We know that a definite total pressure  $P$  corresponds to each temperature; the following values have been found:—

| Temperature | Pressure P |
|-------------|------------|
| 455°        | 27 mm.     |
| 538°        | 81 „       |
| 562°        | 177 „      |
| 586°        | 266 „      |
| 616°        | 401 „      |
| 643°        | 561 „      |
| 670°        | 858 „      |

The aim of the blast furnace is to produce a carboniferous iron by the reduction of oxide ores with the aid of CO. A mix-



ture of much monoxide and little dioxide is obtained by the action of the atmospheric air of the blast on the glowing coal. The sum of the partial pressures of the gas is about 200 mm. Now it is necessary to work so that only the reduction of the oxides takes place during the whole time. For this purpose it is first necessary to have a monoxide concentration sufficiently high compared to the dioxide present, but this condition alone is not sufficient, since we have already seen that in certain circumstances metallic iron itself can be oxidised in presence of pure carbon monoxide. This ought not to take place, especially since a deposition of fine carbon accompanies the oxidation of the metal.

This disturbance is impossible when the sum of the partial pressures of monoxide and dioxide is smaller than  $P$ , the pressure of total equilibrium. We have assumed that 200 mm. is the highest value for the sum of the pressures of monoxide and dioxide in the blast furnace; the table shows that the corresponding temperature is about  $570^{\circ}$ . Thus above  $570^{\circ}$  the re-oxidation of the metal, with its accompanying phenomena, is excluded. The troublesome "scaffolding" in the throat of the blast furnace is obviously caused by a considerable fall in the temperature of the furnace, taking place during normal working, from any cause. When the temperature falls in the zones in which the formation of metal has begun, the equilibrium pressure also falls. The high pressure of monoxide, which is now higher than the pressure corresponding to total equilibrium, causes decomposition of the gas and consequently "scaffolding." The danger is greatest in highly manganiferous iron, since all the equilibrium pressures are lower in this case.

These considerations also enable us to state the factors which determine the composition of the gas in the various zones of the blast furnace. When it is working normally the formation of monoxide occurs near the tuyeres, where the hot blast acts on the glowing coal. The temperature there is so high that the metal and slag melt, so that it is at least  $1100^{\circ}$ . We may assume from this that almost pure carbon monoxide will be formed there. Higher up in the furnace the gases gradually cool down, and become richer in  $\text{CO}_2$ . This is not only due to the reduction, since it is sometimes observed when there are no ores at all in the furnace. The essential influence on the composition of the gases is that exerted by temperature, or by the equilibrium of carbon

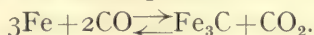
monoxide with the solid carbon, which depends on the temperature. Let us consider a point in field I (Figure 20), and in the part where the pressure is less than that of total equilibrium. Only reduction to metallic iron can take place here, and by carbon monoxide, not by carbon. Thus, in the zones above  $570^{\circ}$ , iron itself takes no part in the reaction, but only helps to bring about more rapidly the carbon equilibrium corresponding to the prevailing temperature; it acts as a catalyte. Owing to the high velocity of the current of gas, the equilibrium  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$  (curve B, Figure 20) is generally not attained, so that the blast furnace gases are always richer in CO than would correspond to the equilibria at the various temperatures of the zones. The carbon produced by the decomposition of CO serves solely to carburise the iron. The temperature gradually approaches that of total equilibrium under the prevailing pressure. There is then equilibrium with the iron. Above this zone a reduction of ferrous oxide to metal can no longer take place, although at these temperatures below  $570^{\circ}$  other reduction processes can occur requiring a smaller monoxide concentration than that required by the reduction of oxide to metal, e.g. the reduction of the higher oxides of iron to ferrous oxide.

Schenck and Falke give the following values for the total equilibrium  $\text{Fe}_3\text{O}_4 - \text{FeO} - \text{C}$  (amorphous):—

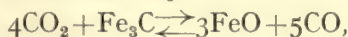
|      |              |
|------|--------------|
| 535° | 129 mm.      |
| 551° | (mean) 175 „ |
| 560° | 303 „        |

It will be seen that the value of 200 mm. for the sum of the partial pressures of  $\text{CO} + \text{CO}_2$  corresponds to a lower temperature (about  $552^{\circ}$  or  $553^{\circ}$ ) than in the case of the total equilibrium  $\text{FeO} - \text{Fe} - \text{C}$ . The reduction of the higher oxide also ceases when the temperature falls below that of complete equilibrium of these substances with carbon and the gases. This last equilibrium determines the composition of the gases escaping from the throat of the furnace. Beyond reduction in the blast furnace there is also absorption of carbon, cementation. We shall see later that this depends on the formation of iron carbide,  $\text{Fe}_3\text{C}$  (cementite), or of solid solutions. We shall also see (cap. V, 6) that the melting-point of iron-cementite alloys is much lower than that of pure iron, the difference in temperature amounting

to about  $400^{\circ}$ . Thus a furnace in which pig-iron is being smelted can be worked at a much lower temperature than one with pure iron, which is very important for the life of the furnace. The occurrence of cementite in the blast furnace is to be explained by a superficial change of Fe into cementite, due to the absorption of carbon from the decomposition of CO ;



On further dissociation of the monoxide  $2\text{CO} = \text{C} + \text{O}_2$ , the carbide is oxidised in a similar way,



until finally total equilibrium is reached between cementite, ferrous oxide, amorphous carbon, and the gas mixture.

Schenck, Heller, Semiller, and Falke found the following data for this equilibrium :—

| Temperature   | P     | % CO | % CO <sub>2</sub> |
|---------------|-------|------|-------------------|
| $468^{\circ}$ | 10.3  | —    | —                 |
| $600^{\circ}$ | 65.0  | —    | —                 |
| $672^{\circ}$ | 131.0 | 86.0 | 14.0              |
| $722^{\circ}$ | 289   | 87.5 | 12.5              |
| $774^{\circ}$ | 562   | 89.5 | 10.5              |

Let us consider in the same way as before the isotherms for a given temperature  $700^{\circ}$ , plotting total pressures as ordinates, and compositions of the gas phase as abscissæ (Figure 21). Beyond the equilibrium curves of Figure 20, Fe—FeO—gas (curve A) and amorphous carbon—gas (curve B), in this case there are two other curves representing the equilibria Fe—Fe<sub>3</sub>C—gas (curve D) and FeO—Fe<sub>3</sub>C—gas (curve C). From the law of mass action we have for the constant  $\mu$  of the first equilibrium (curve D)

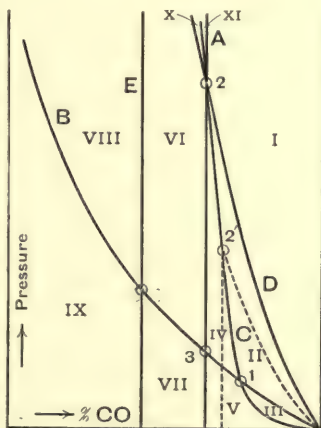


FIG. 21.

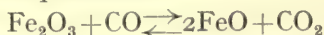
$$\mu = \frac{x^2}{1-x} \cdot P,$$

where  $x$  is the content in CO and  $P$  the total pressure. For the second equilibrium (curve C) we have

$$\delta = \frac{x^5}{(1-x)^4} \cdot P,$$

since four molecules of  $\text{CO}_2$  give five of  $\text{CO}$ .

In Figure 21 the equilibrium



is shown as a straight line E parallel to the ordinate axis. The ratio  $\text{CO} : \text{CO}_2$  is independent of pressure, as in the equilibrium



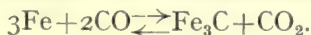
so that both equilibrium isotherms are parallel to the ordinate axis. Only, the equilibrium  $\text{Fe}_2\text{O}_3 - \text{FeO} - \text{gas}$  has a gas phase poorer in  $\text{CO}$ , and its isotherm lies more to the left.

The curve C corresponds to a bivariant equilibrium, since there are three components in three phases; it intersects curve B at point 1, whose co-ordinates P and x can be calculated from the equation

$$\delta = \frac{x^5}{(1-x)^4} \cdot P, \text{ and } \xi = \frac{x^2}{(1-x)} \cdot P.$$

This point represents the univariant equilibrium cementite-- $\text{FeO} - \text{C} - \text{gas}$ , three components in four phases, i.e. at a given temperature the point 1 is exactly defined and there is a definite value of this point for each temperature.

The curve C has another point, 2, where it intersects the straight line A representing the bivariant equilibrium  $\text{Fe} - \text{FeO} - \text{gas}$ , three components in three phases. The point 2 therefore represents the univariant equilibrium  $\text{Fe} - \text{FeO} - \text{Fe}_3\text{C} - \text{gas}$ , three components in four phases. The curve D must also pass through this point, since it represents the bivariant equilibrium



We will now determine the position of this equilibrium point 2, for the temperatures  $650^\circ$  and  $700^\circ$  (Schenck).

$$x = 0.58 \text{ at } 650^\circ$$

$$0.60 \text{ at } 700^\circ$$

and calculating

$$\eta = \frac{x}{1-x}$$

we have  $\eta_{650} = 1.381$ ,  $\eta_{700} = 1.500$ . The values for the system  $\text{Fe}_3\text{C} - \text{FeO} - \text{C} - \text{CO}$  and  $\text{CO}_2$ , which obeys the equation

$$\delta = \frac{x^5}{(1-x)^4} \cdot P,$$

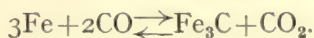


were  $650^{\circ} : P = 95 \text{ mm.} : x = 0.85$   
 $700^{\circ} : P = 222 \text{ mm.} : x = 0.87.$

Hence  $\delta_{650} = 8240$  and  $\delta_{700} = 384,000.$

At the point 2, where equilibrium is complete, the value of  $x$  will be equal in the two equations for  $\eta$  and  $\delta$ , in this particular case naturally equal to the values corresponding to the reduction of FeO by CO to metal and  $\text{CO}_2$ , since the point 2 lies on the line of equilibrium A of this system. Thus in general  $P = \delta \cdot \frac{1+\eta}{\eta^5}$ , hence  $P_{650} = 39,640 \text{ mm.} = 51.6 \text{ atmo.}$   $P_{700} = 126,400 \text{ mm.} = 166.3 \text{ atmo.}$

Obviously, owing to the enormous pressure, this point cannot be reached, though it is of importance, since by its aid we can ascertain the equilibrium-constant  $\mu = \frac{x^2}{1-x} \cdot P$  of the equilibrium



At the point of intersection

$$P = \mu \cdot \frac{1+\eta}{\eta^2}$$

and

$$P = \delta \cdot \frac{1+\eta}{\eta^5}.$$

Since the two values of  $P$  are equal at the point 2

$$\mu = \frac{\delta}{\eta^3}.$$

From the above values of  $\delta$  and  $\eta$  at  $650^{\circ}$  and  $700^{\circ}$ , this equation gives  $\mu_{650} = 31,600$  and  $\mu_{700} = 113,800.$  Using these values we can now calculate the composition  $x$  of the gas in equilibrium with iron and cementite at a given pressure;  $x_{650} = 0.96$ ,  $x_{700} = 0.99.$  Thus at  $650^{\circ}$  and  $700^{\circ}$  iron can be transformed into cementite by mixtures of CO and  $\text{CO}_2$  only when they contain more than 96 or 99 % CO. We can see from the relative positions of curves D and C that ferrous oxide is more easily transformed into cementite than is metallic iron, since at  $650^{\circ}$  the former reaction takes place with 86 per cent monoxide. Since in these cases we are always considering pure cementite, we ought not

to draw the conclusion from these experiments that such a high content of monoxide is required for the occurrence of cementation under all conditions. At certain ranges of concentration and temperature solid solutions (mixed crystals) can be formed between iron and carbide (cf. cap. V, 6), when the conditions are somewhat different. When some carbide dissolves in the iron the two lines A and D representing equilibrium with metallic iron are shifted. In Figure 21 the lines relating to the systems of mixed crystals are shown dotted. The direction of the displacement is found in this way: carbide is readily oxidisable; owing to its presence the solid solution is more readily oxidised than pure iron, i.e. smaller concentrations of carbon dioxide suffice to transform it into ferrous oxide. Thus the line A is shifted to the right, and the point of intersection 2, corresponding to the univariant equilibrium  $\text{Fe}-\text{FeO}-\text{Fe}_3\text{C}-\text{CO}$  and  $\text{CO}_2$ , lies somewhat lower (at 2', Figure 21), i.e. a lower pressure corresponds to the equilibrium mixed crystals —  $\text{FeO}-\text{Fe}_3\text{C}-\text{CO}$  and  $\text{CO}_2$ . Now the cementation curve for the mixed crystals must pass through this point, and therefore it will be shifted to the left, i.e. the cementation of mixed crystals takes place easier than that of pure iron, at a smaller monoxide concentration. Since curve C is very steep, small changes in  $x$  and  $\eta$  will correspond to large shifts of the point 2. Owing to the formation of mixed crystals the point of intersection 3 of the lines A and B, corresponding to the univariant equilibrium  $\text{FeO}-\text{Fe}-\text{C}-\text{CO}$  and  $\text{CO}_2$ , will obviously be lower.

Apart from the formation of mixed crystals, i.e. if we do not consider the dotted curves in Figure 21, we see that the diagram for  $700^\circ$  is divided into eleven fields. Reactions take place in these fields giving characteristic final products. The substances produced are in equilibrium in their respective fields:—

Fields I and XI, cementite and solid carbon.

Fields II and IV, metallic iron and solid carbon.

Fields III and V, metallic iron without separation of solid carbon.

Fields VI and X, ferrous oxide and solid carbon.

Field VII, ferrous oxide without solid carbon.

Field VIII, ferroso-ferric oxide and solid carbon.

Field IX, ferroso-ferric oxide without solid carbon.

Thus at a given temperature all of these four substances can be obtained simply by varying the pressure and the composition of the gaseous phase, consisting of CO and CO<sub>2</sub>.

The occurrence of mixed crystals diminishes fields II, IV, and V, and enlarges fields I, XI, X, VI, and VII. All the fields vary with temperature; since the constants of the curves increase, the fields shift towards the right.

A consideration of these fields shows, above all, that cementite, in contradistinction to the other products, is only stable as an independent phase in those fields in which carbon monoxide is labile and capable of breaking up into carbon and dioxide. It follows from this that cementite can never be formed from metal at the expense of carbon. The only cementation agent by which it can be directly formed is carbon monoxide. However, solid carbon can serve as a cementation agent if cementite is not formed as an independent solid phase, but as mixed crystals; this takes place in field V, in which Fe is the only stable solid phase, assuming that at the given temperature the formation of solid mixed crystals can occur at all. We have mentioned that, for pure iron, fields X and XI cannot be realised owing to the high pressure. However, in the case of manganese and manganiferous iron this is possible since, manganese being less noble than iron, the constants  $\eta$  and  $\delta$  are considerably higher (p. 120). The consequence is that the equilibrium pressures of the systems metal—lower oxide—carbon—gas, and carbide—lower oxide—carbon—gas, and therefore the position of the point 2, will be lowered, to an extent which is roughly proportional to the manganese contained in the iron, *ceteris paribus*; i.e. the point of intersection 2 can be realised for manganese and highly manganiferous ores at temperatures at which this is impossible in the case of pure iron. This is in excellent agreement with practical experience, since a carbide is always obtained by reducing manganese oxide with C and CO, and never a metal free from carbon. Thus in this case manganous oxide is apparently reduced to carbide more readily than to metal, which in the case of iron is first realised at pressures above the point of intersection 2.

## CHAPTER V

### THE APPLICATION OF THE PHASE RULE TO SOLID-LIQUID SYSTEMS

#### 1. The Equilibrium Solid-liquid in Binary Systems Generally.

WHEN three phases of a pure substance such as water are in equilibrium, this equilibrium is invariant. Now the influence of pressure on the equilibrium temperature liquid-solid is very small for almost every substance, and therefore for practical purposes we can identify this invariant point of equilibrium with the freezing-point or melting-point (which are the same if equilibrium takes place) as determined at atmospheric pressure, more especially when the vapour pressure of the components is inconsiderable at the melting-point. Thus the temperature must remain constant during the transformation of the liquid into the solid phase of a pure substance, but this no longer holds when a second substance is dissolved in the liquid phase. By increasing the number of substances the invariant equilibrium becomes univariant. There is a definite temperature of univariant equilibrium for each concentration of the dissolved substance. It is well known that the freezing-point of a pure substance is depressed by the addition of a second substance, and if the two substances do not form solid solutions or compounds the extent of this depression can be calculated by van 't Hoff's formula,\*

$$\Delta t = \frac{0.02 T^2}{Q},$$

or more accurately by Roozeboom's formula,†

\*  $\Delta t$  = lowering of freezing-point by addition of 1 mole;  $Q$  = latent heat of fusion in grm. calories for 1 grm.-mole solvent, i.e., latent heat per grm. solvent multiplied by the molar weight of the solvent.

†  $T_0$  = melting-point of pure substance;  $T_1$  after addition of the second substance;  $\Delta t_1$  = depression of freezing-point when the liquid phase contains  $x$  of the second substance.  $x$  is expressed as a fraction of 1, so that  $x$  has the maximum value of 1 for the second substance pure.



$$T_0 - T_1 = \Delta t_1 = \frac{2T_0 T_1}{Q} \times (-\ln x).$$

The observed deviations from these formulæ are to be explained by the formation of compounds or solid solutions. In the latter case a definite part of the second substance separates out in the solid state together with the solid crystals of the other substance, and the depression of the freezing-point is lower than that calculated by van 't Hoff's formula, or the same depression is produced at higher concentrations than those calculated by Roozeboom's formula. In this case Rothmund's formula holds for the depression of the freezing-point in a hundred moles solvent,

$$T_0 - T_1 = \frac{0.02 T_0^2}{Q} \cdot \frac{C_1 - C_2}{M}.$$

The same symbols are used as before, except that  $T_1$  is that temperature at which a melt with  $C_1$  per cent of the second substance (causing the depression) deposits mixed crystals containing  $C_2$  per cent of this second substance;  $m$  is the molar weight of the dissolved substance or solute.

Let us consider a liquid phase containing two substances A and B, which form neither a compound nor a solid solution, containing, say, 10 per cent of B and 90 per cent of A. On cooling, the first crystals of A will separate at a temperature which can be calculated from the above formulæ. On further cooling, the temperature falls. Owing to the separation of crystals of A the residual liquid becomes poorer in A and richer in B. Crystals of A are again in univariant equilibrium with such a liquid phase at low temperatures. Thus as the temperature gradually falls all possible univariant equilibria between solid A and liquid phases are obtained, until at a definite temperature crystals of B also begin to separate out. At this moment the univariant equilibrium becomes invariant owing to the formation of the new solid phase: as far as freezing is concerned we now have the conditions prevailing in the freezing of a pure solid, i.e. the temperature remains constant till the whole liquid phase has frozen. The concentration of a liquid phase, which, on cooling, is in invariant equilibrium with two substances, is termed the eutectic concentration, and the corresponding constant freezing temperature is the eutectic temperature. The same holds for

the freezing of liquid phases which are rich in B and first deposit B; a series of univariant equilibria are obtained between solid B and liquid phase, till the eutectic concentration and temperature are attained. We will apply these considerations to the technically important Pattinson process.

## 2. The Pattinson Process (Segregation).

This process handles lead which is quite poor in silver and enriches it up to about 2 per cent. The theory of the process

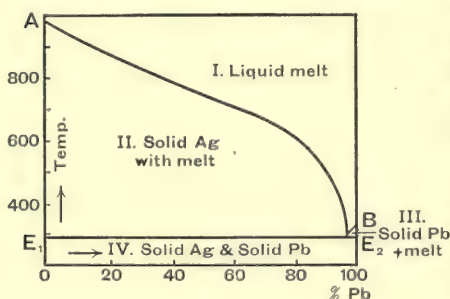


FIG. 22.

is at once clear from the solid-liquid equilibrium diagram given by Petrenko\* for lead-silver alloys (Figure 22).

Taking as ordinates the initial crystallising temperatures, and as abscissæ the corresponding concentrations of the Ag-Pb mixture from 100 per cent Ag (pure

Ag) to 100 per cent Pb (pure Pb), we obtain two curves intersecting at a point, the eutectic point. These curves represent geometrically all the possible univariant equilibria of solid silver or solid lead with a melt. They are the solubility curves of silver and lead (solid), and they are also the curves of crystallisation. Thus on cooling melts from which A separates out first, they pass through a series of concentrations all lying on the branch of the curve starting from A. This goes on till the melt has reached the temperature and concentration of the eutectic point, when the whole becomes solid. On cooling melts from which B separates out first, they pass through all concentrations on the curve starting from B, till they reach the eutectic point and the whole becomes solid.

The diagram in Figure 22 represents all equilibria between solid and liquid, and is divided into four fields by these two curves and by the isotherm  $E_1E_2$  of the eutectic temperature:—

Field I. The whole mixture is liquid.

Field II. Solid Ag coexists with the melt.

Field III. Solid lead coexists with the melt.

\* *Zeitschr. f. anorg. Chemie*, **53**, 200.

Field IV. The two substances can only coexist in the solid state.

Field III is the one of chief technical importance. The lead which is to be worked up only contains a few hundredths per cent of silver, and thus, in the diagram, would lie extremely close to B, the melting-point of pure lead. If this argentiferous lead is melted and allowed to cool slowly, crystals of lead separate out first at a temperature only a little below the melting-point of pure lead, owing to the small Ag content. As the temperature falls still further along the curve starting from B, pure lead crystals still separate out as long as the concentration and temperature of the eutectic point are not yet reached. Petrenko gives  $300^{\circ}$  as the eutectic temperature, at which the composition of the melt is 97.5 Pb and 2.5 Ag.

The Pattinson process is carried out either by lifting out with a perforated ladle the lead crystals separating along the curve starting at B, or by tapping off the still molten lead. The part which remains behind in the former case, or the part which is tapped off in the latter, is a melt which is fairly near to the composition of the eutectic point. The silver content theoretically cannot exceed 2.5 per cent Ag, and in practice this favourable optimum value is never quite reached, since technically the separation has to be effected, not at the eutectic point itself, but at a somewhat higher temperature. Thus under technical conditions we are somewhat to the right of the eutectic point, and a melt is obtained as residue which is rather poorer in silver than the theoretically best yield. It should be mentioned that the unavoidable silver content of the solid lead, which is separated from the melt, is solely due to the adhering mother-liquor, since obviously a quantitative separation of crystals and mother-liquor is technically impossible or unprofitable. But the silver content is not due to the first lead crystals containing silver, as might have been imagined from some of the older descriptions of the Pattinson process. All the processes employed in metallurgy under the name of "segregation" work on the same principle as the Pattinson process.

### 3. Occurrence of Solid Compounds in Binary Systems. The Transition Point.

When two substances A and B form a compound  $A_nB_m$ , we obtain a new curve in our phase diagram which corresponds to



the univariant equilibrium between the compound  $A_nB_m + \text{melt}$ . But we have to distinguish two cases, according to whether the compound melts homogeneously (Figure 23, I), or with the deposition of one of the components (Figure 23, II). In the

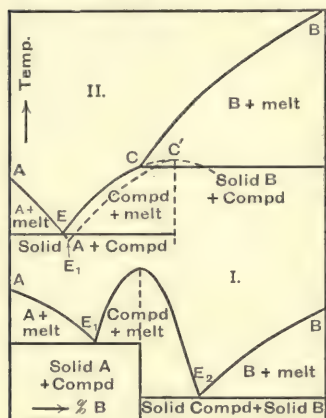


FIG. 23.

former case the curve of the compound shows a maximum melting-point with two eutectic points  $E_1$  and  $E_2$ . In the latter case the equilibrium curve of compound and melt intersects the equilibrium curve of the pure substance B at the point C. This is termed the transition point of the compound, which means that above this temperature the substance B, and below it only the compound, is in equilibrium with the melt. In melts of concentrations within the range C-B at the temperature of the transition point, the crystals

of B, which separate out first, change into the compound at constant temperature with the evolution of heat. This change can be observed experimentally by introducing a thermometer into a melt of a concentration in the range C-B and observing a halt on cooling, due to the separation of the eutectic, as in the freezing of a pure substance, when the halt is due to the separation of the pure solid. The duration of this halt will be a maximum for a melt in which the amount of the compound formed is a maximum, which is the case when the two substances are present in the melt in amounts corresponding to the composition of the compound. This maximum halt at a given temperature can be taken as a criterion for the composition of the compound; in the case of homogeneous melts the position of the maximum melting-point indicates the composition of the compound in question. The fields of existence of the single phases are obvious from the description of Figure 23, I and II. Clearly two substances may form two or more compounds with a maximum melting-point or a transition point. Thus Schenck \* detected three compounds in the binary system

\* R. Schenck, *Berichte*, **41**, 2917.



PbO and  $\text{PbSO}_4$ : the compound  $\text{PbSO}_4, \text{PbO}$  melts homogeneously at  $966^\circ$  and  $\text{PbSO}_4, 2\text{PbO}$  at  $951^\circ$  [the former plays some part in lead roasting (IV, 4)]; lastly, there is a compound  $\text{PbSO}_4, 3\text{PbO}$  with a transition point at  $880^\circ$ , which, according to what we have said above, will decompose above this temperature into  $\text{PbSO}_4, 2\text{PbO} + \text{melt}$ . Accordingly three eutectic points are found in this system.

Between  $\text{PbO}$  and  $\text{PbSO}_4, 3\text{PbO}$  at  $820^\circ$  (87 % PbO)

„  $\text{PbSO}_4, 2\text{PbO}$  and  $\text{PbSO}_4, \text{PbO}$  at  $940^\circ$  (53 % PbO)

„  $\text{PbSO}_4, \text{PbO}$  and  $\text{PbSO}_4$  at  $950^\circ$  (30 % PbO).

It should be added here that all these considerations on two-component systems hold for any two substances, for two metals, salts, oxides, sulphides, organic substances, or finally, for systems of salts and water. Hitherto we have only been thinking of equilibrium conditions, apart from supercooling or similar phenomena such as those mentioned in II, 9. Thus in Figure 23, II, the compound which is in stable equilibrium along EC may first separate out in the range CB by the curve EC becoming prolonged towards  $C_1$ . The compound in question, say a salt hydrate, is in unstable equilibrium along  $CC_1$ . This unstable hydrate then turns spontaneously, say through the action of nuclei, into the stable system, melt + anhydrous salt B. Ostwald has formulated a general law, that of successive stages, which states that of several possible reactions, the one which takes place first will be that which gives rise to substances in unstable equilibrium. These only turn into stable systems subsequently. Thus a salt solution may first deposit an unstable hydrate in the range EC instead of the stable hydrate lying upon the curve EC, the stable form only being formed subsequently. An unstable solubility curve  $E'C'$  with an unstable transition point  $C'$  corresponds to the unstable hydrate. The position of the unstable solubility curves  $CC'$  and  $E'C'$  in Figure 23, II, show that at the same temperature the solubility of the unstable form must always be greater than that of the stable form. Thus when we mix with water a salt (substance B) which can form hydrates, reactions will occur which can give stable or unstable hydrates, depending on the conditions of concentration and temperature. The unstable will then be transformed secondarily into the stable form, frequently with a relatively small reaction-velocity. These

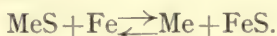
facts are of special importance for the theory of hydraulic binding agents, which we will consider in cap. VI. For the moment we will return to the reactions occurring in the melt, i.e. in the homogeneous phase, when a compound is produced. For the purpose of the phase rule, compounds of two substances represent an independent component, like the single pure substances A and B which go to form it. It should be noted first that addition of A or B depresses the melting-point of the pure compound AB according to the van 't Hoff formula (cap. V, 1), just as on the first addition of A to B or B to A. Thus the maximum melting-point of the compound C should be given by the sharp point of intersection of the two solubility curves of the compound C in the substances A and B. Experience shows that instead of a sharp point, a more or less rounded maximum is observed. This is because most of such homogeneously melting compounds melt with dissociation, i.e. there is the equilibrium  $AB \rightleftharpoons A + B$  in the liquid phase. The first addition of A or B mainly goes to disturb the equilibrium, since, according to the law of mass action, excess of one component throws back the dissociation. In this way the greater part of the first addition is consumed in re-forming the compound, and only a small part of it can act as a foreign substance, lowering the melting-point. This explains the very small depression of the melting-point in the case of such compounds on the addition of a comparatively rather large initial excess of one or the other component, and also the rounding-off shown at the maximum melting-point of such compounds.\* This dissociation in the melt is a final reason for the occurrence of a transition point, instead of a homogeneous melting-point, in the case of a compound. When one component B, which is present as such in the melt owing to dissociation, has a smaller solubility than the undissociated compound, it separates out at first instead of the compound, and thus gives rise to a transition point. The dissociation of molten compounds, e.g. of sulphides, is of technical importance. It can be seen that sulphides are dissociated in the molten state, e.g.  $FeS_2 \rightarrow Fe + S_2$ , from the fact that it is possible actually to distil off the sulphur from pyrites on the principle of the dis-

\* The dissociation at the melting-point can be calculated approximately from the extent of the rounding-off. Cf. R. Kremann, *Z. f. Elektroch.*, 1906, 12, 259.

turbance of equilibrium. The sulphides of the metals show considerable differences in their degree of dissociation, and this fact is the theoretical basis of the iron-reducing method.

#### 4. The Iron-reducing Method and the Formation of Matte.

This method consists in heating the sulphides of valuable metals with iron, when the metal is liberated and the sulphur combines with the iron,



The reaction is more or less complete according to the position of this equilibrium. In many cases the reaction is favoured by the metal Me forming a second stable liquid phase and being thus removed from the equilibrium, so that fresh metal can be continually formed until a complete equilibrium has resulted. On the other hand, it may happen that the two sulphides form compounds, or solid solutions, or both. The possible extent of desulphurisation depends a great deal on the proportions of sulphide and metal. It is also important to know the mutual behaviour of the two metal sulphides. The alloys which they form are termed "mattes," and the most important technically are those of lead, copper, and nickel.

The desulphurisation of lead by the iron-reducing method is effected by smelting lead sulphide with materials rich in iron oxide (pure iron would be too dear) at a high temperature, at which metallic iron is first formed in the shaft furnace. The reduction then takes place according to the equation  $\text{PbS} + \text{Fe} = \text{Pb} + \text{FeS}$ . The slag resulting from the added materials flows off, while the metal and the lead matte collect in the hearth of the furnace. The lead matte consists of solid PbS and solid FeS; no compound or solid solution is produced, since the phase diagram shows only two melting curves with one eutectic point. K. Friedrich\* gives  $863^\circ$  as the eutectic temperature with the composition 70 % PbS and 30 % FeS; the melting-point of pure PbS is  $1114^\circ$  and of FeS  $1187^\circ$ . The lead matte obtained in practice also contains copper, and after roasting it is again used in the reduction; thus the matte becomes gradually poorer in lead and richer in copper, so that at last the so-called copper matte is obtained. This is then used like other copper ores or,

\* *Metallurgie*, 1907, 4, 479.



more correctly, with other copper ores, to yield copper by roasting and smelting to black copper. The so-called crude matte which is worked up always contains rather large amounts of FeS, which is comparatively difficult to remove, since it is not present in copper matte as such, but in the form of different compounds. The researches of P. Röntgen\* show that FeS (M.P.  $1133^{\circ}$ ) and  $\text{Cu}_2\text{S}$  (M.P.  $1085^{\circ}$ ) form the following three compounds:—

|   |                     |
|---|---------------------|
| $(\text{Cu}_2\text{S})_3, \text{FeS}$     | M.P. $1065^{\circ}$ |
| $\text{Cu}_2\text{S}, \text{FeS}$         | M.P. $1030^{\circ}$ |
| $(\text{Cu}_2\text{S})_2, (\text{FeS})_5$ | M.P. $980^{\circ}$  |

In presence of three homogeneously melting compounds four eutectic points are required by theory, and of these Röntgen obtained the following:—

$\text{Cu}_2\text{S} - (\text{Cu}_2\text{S})_3, \text{FeS}$  at  $995^{\circ}$  and 78.2 %  $\text{Cu}_2\text{S}$  and 21.8 FeS.

$(\text{Cu}_2\text{S})_3, \text{FeS} - \text{Cu}_2\text{S}, \text{FeS}$  at  $1000^{\circ}$  and 67 %  $\text{Cu}_2\text{S}$  and 33 FeS.

$(\text{Cu}_2\text{S})_2, (\text{FeS})_5 - \text{FeS}$  at  $895^{\circ}$  and 33 %  $\text{Cu}_2\text{S}$  and 67 FeS.

In obtaining metallic nickel the raw materials, nickeliferous magnetic ore and pyrites, are smelted to a matte in the same way as copper sulphide ores. On roasting they yield a mixture of sulphides, oxides, and sulphates of iron, nickel, cobalt, and copper. The roasted material is subjected to a reducing smelting in a shaft furnace with coke and suitable materials. The iron-reducing process then takes place, and part of the ferrous sulphide forms a crude matte with the nickel sulphide usually containing some copper, while the other part of the iron passes into the slag with the cobalt. The crude matte is then further worked for nickel.

The phase diagram of the two substances shows that nickel sulphide can be practically completely removed from the iron sulphide in the crude matte. The phase diagram given by Bornemann† is very different from those we have considered so far, since the compound produced,  $(\text{FeS})_2, \text{Ni}_3\text{S}_2$ , forms solid solutions with the two components FeS and  $\text{Ni}_3\text{S}_2$ . Before discussing this system we must briefly consider the typical case of the binary phase diagram when solutions are produced, together with some useful examples.

\* *Metallurgie*, 1906, 3, 479.

† *Metallurgie*, 1908, 5, 61.



### 5. Solid Solutions (Isomorphous Mixtures) in Binary Systems. Nickel Matte.

Two liquids may be completely miscible, i.e. in all proportions, or only partially miscible, i.e. there is a gap which may be large or small. In the same way solid solutions may exhibit complete miscibility or may show gaps. When there is complete miscibility the solid-liquid equilibrium curve connects the melting-points of the two components, usually lying concave to the concentration axis (Roozeboom's Type 1). Taking a melt of composition C (Figure 24), this will first deposit mixed crystals (composition C') richer in the component B of higher melting-point. But, if equilibrium takes place, the mixed crystals, which separated out first, interact with the melt, as the temperature falls on further abstraction of heat, giving crystals poorer in B. At a temperature corresponding to a point D the whole mass becomes solid. The

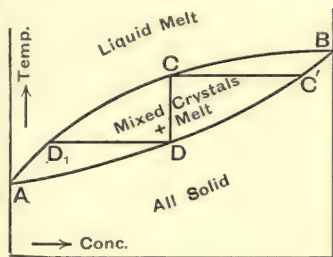


FIG. 24.

crystals corresponding to the point D will be in equilibrium with a melt  $D_1$ . Similar considerations apply for all other points. ACB, the initial freezing curve, and ADB, the final freezing curve, divide the area into three fields:—

Above ACB. Liquid melt.

Between ACB and ADB. Liquid melt in equilibrium with mixed crystals.

Below ADB. All solid.

It should be noted that the initial freezing curve may also show a maximum (Roozeboom's Type 2) or a minimum (Roozeboom's Type 3).<sup>\*</sup> When there is a gap in the series of mixed crystals in the solid state two cases can be distinguished:—

- (a) There is a transition point lying between the freezing-points of the components, in the limiting case at the freezing-point of the lower-melting component. (Roozeboom's Type 4.)

<sup>\*</sup> See Ruer, *Metallographie*; Kremann, *Anwendungen der thermischen Analyse zur Erkennung chemischer Verbindungen* (Ahrens' Sammlung).

- (b) There is a eutectic point lying below the freezing-point of either pure component. (Roozeboom's Type 5.)

In either case there are two sorts of mixed crystals. Let us consider what happens in the case of Roozeboom's Type 4 (Figure 25). The mixed crystals  $\alpha$  are those which separate out

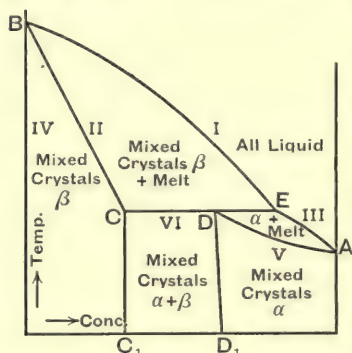


FIG. 25.

from a melt richer in A. In a state of equilibrium they can only take up a limited amount of B: when they have taken up this maximum of B they are the limiting mixed crystals D, saturated with B; on the other hand, mixed crystals  $\beta$  rich in B separate out from melts rich in B, and in the limiting case they take up as much A as corresponds to the point C. The range of concentrations between C and D represents the gap in the solid series

of mixed crystals. The initial freezing curve is composed of two curves, BE and EA, intersecting at E, which lies between the freezing-points of the two components. Along EA the mixed crystals  $\alpha$  separate out first, along BE the mixed crystals  $\beta$ . Both kinds of mixed crystals are in equilibrium with the melt at the point E only. This is a transition point (cf. p. 136) since above it mixed crystals  $\beta$ , below it mixed crystals  $\alpha$ , are in equilibrium. If the melts from which mixed crystals  $\beta$  separate out are richer in A than corresponds to the point C (i.e. are to the right of the ordinate of the point C), then as soon as the temperature falls to that of the transition point E (i.e. to the horizontal line CDE), all the mixed crystals  $\beta$  have the composition of the limiting mixed crystals C richer in B, and interact with the remainder of the melt to give limiting mixed crystals D richer in A:—



These changes occur with evolution of heat and can be experimentally followed with a thermometer placed in the melt as it is cooling. The maximum change occurs in a melt corresponding to the point D. The position of this point may be ascertained by the fact that the temperature remains constant for

a maximum time there. Thus we have the following fields of existence :—

Field I. Liquid melt.

Field II. Mixed crystals  $\beta$  + melt.

Field III. Mixed crystals  $\alpha$  + melt.

Field IV. Only mixed crystals  $\beta$ .

Field V. Only mixed crystals  $\alpha$ .

Field VI. Only mixed crystals  $\alpha$  and  $\beta$  together, of the composition of the saturated limiting mixed crystals D and C.

We will make a practical application of this case to the system  $\text{Zn}-\text{Ag}_2\text{Zn}_5$ , which is of importance technically in the Parkes process.

In the extreme case the gap between the series of mixed crystals may extend as far as one of the components, usually that of lower melting-point; in this case the points E and D coincide with A, i.e. the limiting mixed crystals D, rich in A, are identical with the pure component A. Fields III and V vanish, and fields II and VI are limited by the point A or its ordinate.

This latter case, combined with Roozeboom's Type 1 (complete miscibility of components), occurs in the binary system  $\text{FeS}-\text{Ni}_3\text{S}_2$ , nickel matte. These components form a compound  $(\text{FeS})_2, \text{Ni}_3\text{S}_2$ , so that there are two binary systems :—

System  $\text{FeS}-(\text{FeS})_2, \text{Ni}_3\text{S}_2$  . . . . . I, Figure 26

and System  $(\text{FeS})_2, \text{Ni}_3\text{S}_2-\text{Ni}_3\text{S}_2$  . . . . . II, Figure 26.

The first system (I) belongs to Roozeboom's Type 4, with the special peculiarity which has been mentioned already, that the gap CD in the series of mixed crystals reaches right down to the lower-melting component  $(\text{FeS})_2, \text{Ni}_3\text{S}_2$ .

The second system (II) exhibits complete miscibility in the solid state and thus belongs to Roozeboom's Type 1. This complicated behaviour of the alloys in the

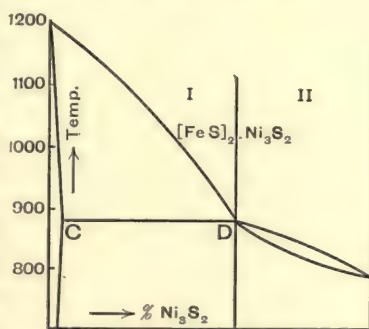


FIG. 26.

matte makes it difficult to treat theoretically the separate reactions in the iron-reducing process.

We may return for a moment to the second case of the forma-

tion of solid solutions with a gap in the series of solid phases, Roozeboom's Type 5 of isomorphous mixtures; it occurs in the important case of steel.

Figure 27 is an equilibrium diagram for Type 5. The equilibrium curve solid-liquid, i.e. the initial freezing curve, is given

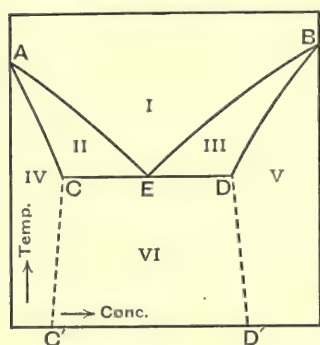


FIG. 27.

by the curves AE and EB, intersecting at the eutectic point E. Along AE mixed crystals  $\alpha$  separate out which are rich in A, and poorer in B than the melt; along BE mixed crystals  $\beta$  separate out which are rich in B and poorer in A than the melt. The gap in the solid series of mixed crystals extends from C to D, i.e. the mixed crystals  $\alpha$  (rich in A) can only take up B till they reach the point C as a maximum, while the mixed crystals  $\beta$  (rich in B) can only dissolve as much A in the solid state as corresponds to the point D. The course of the curves AE, BE can be calculated from Rothmund's formula (cap. V, 1). When the temperature falls to the eutectic point, a melt inside the range of concentration CD freezes at constant temperature to a conglomerate of the two limiting mixed crystals C and D. The point E is an invariant equilibrium at which the two kinds of mixed crystals  $\alpha$  and  $\beta$  separate out simultaneously. Remembering that CC' and DD' represent the change in the range of immiscibility with falling temperature, as in Type 4 (Figure 25), we have:—

Field I. Liquid melt.

Field II. Mixed crystals  $\alpha$  in equilibrium with melt.

Field III. Mixed crystals  $\beta$  in equilibrium with melt.

Field IV. Solid mixed crystals  $\alpha$ .

Field V. Solid mixed crystals  $\beta$ .

Field VI. Solid mixed crystals  $\alpha$  and  $\beta$  together. The composition is that of the limiting mixed crystals C and D.

With a knowledge of the fields of equilibrium of these various types we may now discuss the alloys of carbon and iron.



### 6. The Alloys of Carbon and Iron.\* Puddling.

Before discussing the equilibrium diagram which the most recent work has established for Fe—C alloys, we must first mention several remarkable peculiarities. First, solid iron can exist in stable equilibrium in three different polymorphic modifications according to the temperature. The point at which two such polymorphic modifications are in equilibrium with vapour (which is obviously at an excessively low pressure in this case) is a triple point; the equilibrium is invariant, since three phases (two solid and one gaseous) of the same substance are coexisting. It is

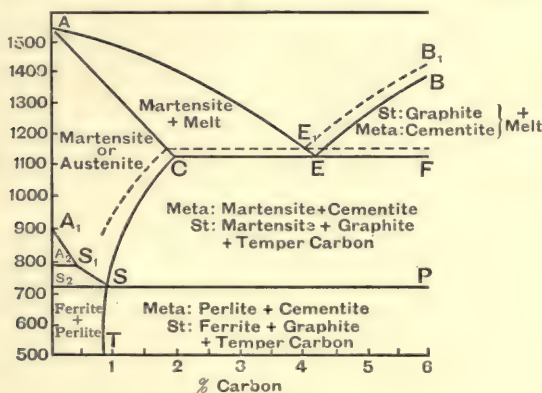


FIG. 28.

a transition point; above it only one, below it only the other, polymorphic modification can exist in univariant equilibrium. If to one of these polymorphic modifications at the transition point we add another substance, such as iron carbide,  $\text{Fe}_3\text{C}$ , the equilibrium becomes univariant instead of invariant, and the transition point is lowered to an extent proportional to the amount of carbon dissolved in the solid state, in the same way that the solid-liquid equilibrium point of a single substance is lowered by adding a second substance. According to the recent researches of Carpenter and Keeling,  $\gamma$  iron separates out first from liquid pure iron at  $1505^\circ$  (A, Figure 28). At  $900^\circ$  (A<sub>1</sub>,

\* P. Goerens, *Vorgänge b. d. Erstarrung u. Umwandlung v. Eisenkohlenstofflegierungen u. s. w.* Benedicks, *Über d. Gleichgewicht u. d. Erstarrungsstrukturen d. Systems Eisen-Kohlenstoff*, pub. W. Knapp, Halle, 1907. Also Schenck, *Chemie d. Metalle*, p. 67 et seq.

Figure 28) this undergoes a change into  $\beta$  iron. At  $760^\circ$  ( $A_2$ , Figure 28) the latter is in stable equilibrium with the third polymorphic modification,  $\alpha$  iron, called "ferrite" in metallurgy. The curves  $A_1S_1$  and  $S_1S$  (Figure 28) show the same change in transition point on increasing the carbon content.

Secondly, we must emphasise the fact that in the Fe—C alloys there are two phase diagrams to be considered, one stable and the other metastable. In metastable equilibrium, alloys above 4.2 % C deposit cementite (iron carbide) from the melt, but in stable equilibrium this carbide dissociates, giving carbon. This is another example of Ostwald's law of successive stages (cf. cap. V, 3). Goerens states that the unstable cementite always separates out first, giving the stable graphite secondarily. We may add that the dissociation proceeds more readily the richer the melt is in carbon, so that the cementite curve cannot be followed right up to the melting-point of cementite (6.67 % C).

We will consider first the stable and metastable iron-carbon system as far as the point of the composition  $Fe_3C$  (6.67 % C) pure cementite.

Mixed crystals of iron and carbon, or probably more correctly of iron and  $Fe_3C$ , separate out along AE. These mixed crystals are called martensite, those richer in carbon austenite; they become solid below AC. C is the limit of solubility of carbon in iron, and corresponds to the saturated mixed crystals of Fe and  $Fe_3C$ . E is the eutectic of the mixed crystals (martensite or austenite) and pure cementite. At the temperature of the horizontal CEF, liquid phases richer in carbon than the point C become solid by the whole melt freezing to a conglomerate of martensite and cementite crystals. Owing to the transformation phenomena in the iron there is a limitation of the field, in which martensite or austenite is in metastable equilibrium, by the curves  $A_1S_1$  [equilibrium between mixed crystals of cementite in  $\gamma$  iron and mixed crystals of cementite in  $\beta$  iron] and  $SS_1$  [equilibrium between  $\alpha$  iron (ferrite) and cementite crystals]. The curve connecting S and C is the solubility curve of cementite in  $\gamma$  iron as the temperature falls. We have:—

Field  $ACSS_1A_1$ . Mixed crystals of cementite and  $\gamma$  iron.

Field  $A_1S_1A_2$ . Mixed crystals of cementite and  $\beta$  iron.

Field  $A_2S_2S_1S$ . Mixed crystals of cementite and  $\alpha$  iron.

The solubility of cementite in  $\alpha$  iron is very small; below the temperature of S,  $710^\circ$ ,  $\alpha$  iron dissolves no cementite at all and martensite or austenite dissociate into  $\alpha$  iron and cementite. S corresponds to 0.81 per cent carbon and is the eutectic temperature of the solid solutions; it is a triple point at which the two components Fe and  $\text{Fe}_3\text{C}$  coexist in the three solid phases, ferrite, martensite, and cementite. Below the temperature of S, i.e. below the isotherm  $\text{S}_2\text{SP}$ , only ferrite and cementite coexist. The eutectic crystalline conglomerate of ferrite and cementite is a special mechanical structural element, and is called perlite. Melts poorer in carbon than S, below  $710^\circ$  (the temperature of the horizontal  $\text{S}_2\text{SP}$ ), contain ferrite and perlite in the field  $\text{SS}_2\text{T}$ , while melts richer in carbon than S contain cementite and perlite in the field  $\text{STP}$ ; in either case the equilibrium is metastable. We may also mention that  $\text{CEFPS}$  is the field of coexistence of mixed crystals of  $\gamma$  iron with cementite, i.e. of cementite and martensite, while  $\text{BEF}$  is the field of the metastable mixture of cementite with the melt. Crystals corresponding to the metastable equilibrium are obtained by rapidly cooling the system to such a low temperature that the reaction-velocity of the change into the stable system is very low, e.g. by plunging into water. If the system is cooled slowly, so that the iron-carbon alloys remain long enough in the temperature range of higher reaction-velocity, the cementite splits off carbon in the form of graphite. When the graphite is allowed to freeze out of an iron-carbon alloy as a stable system the solubility must be lower (p. 137) than when cementite separates out as the solid phase: the equilibrium curve for graphite melt thus lies as shown by the dotted curve  $\text{B}_1\text{E}_1$ . Therefore, when cementite breaks up in the field  $\text{EBF}$ , this field contains graphite in stable equilibrium with the melt. The graphite formed in this field is in large scales, and is not the ordinary form, as it differs from the finely divided graphite which is separated from the metastable cementite in the field  $\text{CSPFE}$  as a portion of the texture of the eutectic E. The cementite of the eutectic E, which breaks up below  $1130^\circ$  (the temperature of the line  $\text{CEF}$ ), gives a finely divided graphite called temper carbon, so that in the field  $\text{CSPFE}$  we have graphite, temper carbon, and mixed crystals in stable equilibrium, and in the field below  $\text{S}_2\text{SP}$  we have graphite, temper carbon, and ferrite in stable equilibrium.



We will leave out of consideration for the moment the influence of foreign substances (Si, Mn, Cr, Wo, etc.), and assume that the hardness of the iron obtained from the molten metal is determined by its content in cementite or the mixed crystals of cementite with iron. Rapid cooling, by plunging in water, gives a hard metal, which contains mixed crystals only, or cementite also, according as to whether the carbon content is low (steel) or high (white pig-iron). In the former case the iron can still be mechanically worked; in the latter it is usually too brittle.

If we allow it to cool slowly, giving it the opportunity of changing into the stable system, we obtain a system, grey pig-iron, consisting of ferrite, graphite, and temper carbon, which is comparatively soft owing to the lack of cementite and its mixed crystals. If the molten metal is first cooled slowly and then, below  $1130^{\circ}$ , rapidly, we can obtain mixed crystals of iron and cementite, together with graphite and temper carbon; further, with a suitable velocity of cooling which still does not allow of the dissociation of cementite, we can obtain from iron poorer in carbon than 4.2 per cent a mixture of ferrite and perlite, and from an iron richer in carbon than 4.2 per cent a mixture of perlite and cementite. This shows what different sorts of iron or different structural elements can be obtained according to the method of cooling. We may say in general that plunging into water hardens the material, while tempering i.e. heating the solid solution  $\text{Fe}-\text{C}$  to a rather high temperature lowers the hardness, since at rather high temperatures the reaction-velocity of the change of the metastable into the stable system is raised, and the stable system corresponds to a less degree of hardness. The temperature of tempering will determine the kind of crystals in stable equilibrium at that temperature, and the amount of these crystals will increase with time.

E. Heyn\* remarks how instructive are the processes which take place in the manufacture of wrought iron in puddling furnaces and after making the blooms,† until they cool. The molten mass in the puddling furnace, of a given carbon content, corresponds to a point in the field of liquid melts above AE (Figure 28). The carbon content of the mass is reduced under the influence

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\* *Die Metallographie im Dienste der Hüttenkunde*, 1903.

† Lumps of iron worked up with slag, about 19 or 20 lbs.



of the refining action of the slag and of the furnace gases until, after some time, it reaches a concentration corresponding to the temperature of a point on the curve AE. Let us call this carbon content  $\rho$ , corresponding to the separation of the first crystals at a given temperature. We ascertain the composition of the mixed crystals separating out at this temperature in the manner explained above, by drawing a parallel to the concentration axis from the point  $\rho$  of the curve AE<sub>1</sub>E (Figure 28) as far as the curve of complete freezing AC, when the point of intersection  $\phi$  gives the composition of the mixed crystals which separate out. Their absolute amount is practically zero on reaching the concentration  $\rho$  in the melt. Let us assume that during the refining process the temperature in the puddling furnace remains constant\*; on further refining, the carbon content of the whole bath will continue to fall below the point  $\rho$ , and thus mixed crystals  $\phi$  in increasing amount coexist with mother-liquor  $\rho$  in decreasing amount. Thus, from the moment when the first crystals come out, the ratio between crystals (composition  $\phi$ ) and the mother-liquor (composition  $\rho$ ) rises steadily from zero. The separation of these crystals from the liquid mother-liquor is a well-known phenomenon in puddling and is visible to the eye. The composition of the crystals does not change, and their carbon content is equal to the abscissa of the point  $\phi$ . The carbon content of the mother-liquor  $\rho$  also does not change, and the sole change is in the ratio of crystals to mother-liquor, which is in favour of the former. Finally, on still further refining, the whole bath reaches the carbon content of the crystals (point  $\phi$ ), i.e. the whole alloy is now changed into solid mixed crystals and the amount of the liquid mother-liquor has become zero. The separate mixed crystals do not form a solid mass, but are separated by particles of slag with which they form a paste; the refining action thus still goes on. The carbon content of the crystals corresponds with points in the martensite field (Figure 28) of a certain carbon content, which becomes smaller and smaller the longer the refining process is continued. Naturally, as soon as we reach the martensite field, the carbon content is only an average value, because the various mixed

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\* This is not true, but the deviations owing to change of temperature will not essentially affect our conclusions as a whole.

crystals are not homogeneously refined and differ in carbon content. The blooms are removed from the furnace when the average carbon content has reached the desired value. As they are worked further the temperature falls without causing a change in carbon content, but only causing different structural changes; as we showed above, these depend on the velocity of cooling. Puddling is thus particularly instructive, since it exhibits to the eye the separation of a liquid system into crystals and mother-liquor within the field lying between the curves  $AE_1E$  and  $AC$ .

The properties of iron-carbon alloys may be changed in two ways by foreign substances. First these may act as accelerating or retarding catalytes on the dissociation of cementite, and, secondly, they may shift the transition temperature and the eutectic point, and thus the boundaries of the mixed crystal field. Silicon accelerates the dissociation of cementite and depresses its solubility in iron. Manganese acts in the reverse direction, making the metastable carbide more stable. We can understand this by remembering that the manganese cementite  $Mn_3C$  corresponding to  $Fe_3C$  is a stable compound (cf. p. 131), which thus does not dissociate spontaneously into its elements. Now these two cementites are completely miscible in the solid state. It is generally assumed that the properties of isomorphous mixtures, e.g. their power of resistance, are made up approximately additively from the properties of their components. Thus manganese carbide, with its low tendency to dissociate into its elements, imparts this property to manganiferous iron-carbon alloys. This is in accordance with the fact that white pig-iron, which is rich in cementite, always contains more or less manganese, while grey pig-iron, which is poor in cementite, contains silicon.

Nickel can form mixed crystals in all proportions with both  $\gamma$  and  $\alpha$  iron; it enlarges the martensite field  $ACSS_1A_1$ , and lowers not only the eutectic point  $S$ , but also the transition points  $A_1$  and  $A_2$  of the iron;  $A_1$  is lowered relatively more than  $A_2$ , so that with large amounts of nickel  $A_1$  vanishes, when a direct transformation of  $\gamma$  into  $\alpha$  mixed crystals can be observed.

On the other hand, chromium and tungsten, like silicon, favour the formation of  $\alpha$  ferrite, with which they form mixed crystals. They have not the power of passing into the martensite, but

they raise the eutectic perlite point  $S$ , and diminish the stable field of  $\gamma$  mixed crystals. The presence of these different metals in the field of  $\gamma$  mixed crystals  $ACSS_1A_1$  has a similar effect to an increase in the content of cementite ; they exert a hardening action, since, as we mentioned above, the mixed crystals are harder than the softer components. These particular steels, especially nickel steel, have the advantage over a pure iron-carbon steel that, although hard, they are not brittle. The stability of the mixed crystals is especially high in the case of quaternary steels, in which two metals such as chromium and tungsten are added to the iron-carbon mixture. When these steels have been subjected to a very high temperature before cooling, they need not be plunged in water to make them hard, i.e. rich in cementite, as they are practically not transformed at all into the more stable perlite form. In a pure carbon steel the dissociation of cementite with loss of hardness takes place rapidly by heating to  $600^\circ$ . But for chromium and tungsten steel this transformation into the perlite form can only be effected by heating to  $700^\circ$  for at least one hour. Thus these steels are especially suitable for tool steels, e.g. for drilling or turning, since with them there is not the same fear of losing temper when running hot.

## CHAPTER VI

### TRANSFORMATION PHENOMENA IN HYDRAULIC BINDING AGENTS \*

#### 1. Hydrates of Calcium Sulphate.

THE iron-carbon alloys furnished examples of the transformation phenomena of labile (metastable) modifications into the stable form and of the influence of foreign substances on these changes. We will now consider similar phenomena connected with the setting of hydraulic binding agents.

We will first consider gypsum, and before discussing its setting we will examine the process of dehydration, which yields modifications of technical importance. The technical starting-point for the various kinds of gypsum is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , the dihydrate of calcium sulphate. Like all salts containing water of crystallisation, this salt even at ordinary temperatures exerts a definite vapour pressure, which increases on heating, as the vapour pressure of pure water increases with rising temperature. But while the vapour pressure curve of water (II, Figure 29) does not rise very rapidly, that of the dihydrate (I, Figure 29) is steeper, so that the two curves intersect at a point U.

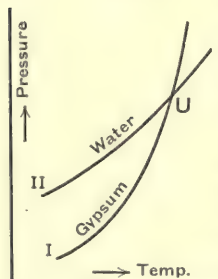


FIG. 29.

Working in a closed vessel, i.e. when water cannot escape, this means that at  $107^\circ$  the vapour pressure of the dihydrate is equal to that of water, while above this temperature it is higher than that of water; thus if the dihydrate is heated in a closed vessel above  $107^\circ$  water condenses from it, i.e. the gypsum dissociates into a hydrate poorer in water, the hemihydrate  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (plaster of paris) and water.  $107^\circ$  is the only temperature at which

\* Rohland, *Stuck-u. Estrichgips*, pub. Quandt and Händel, 1904.



dihydrate and hemihydrate can coexist in equilibrium ; this temperature is therefore of practical importance, since the gypsum burner uses this transformation to obtain burnt gypsum, i.e. plaster of paris ; in this case, however, he is working under atmospheric pressure and obtains the water as steam. Theoretically a temperature only slightly above  $107^{\circ}$  would be sufficient ; but in practice a higher temperature is employed, over  $130^{\circ}$ , mainly because the reaction-velocity just above the transition point would be too small. Apart from the influence of rise in temperature, which increases the reaction-velocity of every reaction and transformation (cf. cap. II, 1), the reaction-velocity of the transformation of the unstable into the stable phase is in itself greater the higher the temperature is above the transition point. On further heating there is another transition point at  $130^{\circ}$ , that of the transformation of the hemihydrate, plaster of paris, into anhydrous gypsum. It should be noted that this is another example of Ostwald's law of successive stages, according to which the unstable form is produced first, and then turns into the stable form. The existence of plaster of paris is an excellent example in proof of this law. When the dihydrate is heated to  $130^{\circ}$ , water and an anhydrous form should be produced in stable equilibrium. However, we observed that the hemihydrate  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  is produced first, which, though unstable, nevertheless has a certain degree of stability. It only evolves water after rather a long time, giving a mixture of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaSO}_4$ .

The instability of the hemihydrate explains the fact that the dihydrate often occurs in nature in direct contact with anhydrite, while the hemihydrate does not occur naturally ; we will use this fact in considering the hydration and hardening of different kinds of gypsum. The anhydrous modification formed above  $130^{\circ}$ , which Rohland calls  $\text{CaSO}_4\text{a}$ , is dead-burnt gypsum, which possesses the power of taking up water, but not of hardening without further treatment. It appears to be an unstable polymolecular modification of  $\text{CaSO}_4$ . On heating  $\text{CaSO}_4\text{a}$  to a rather high temperature,  $525^{\circ}$ , it appears to dissociate into simpler molecules with a measurable velocity, giving, according to Rohland, " b," which differs from modification " a," dead-burnt gypsum, in possessing not only the power of hydration, but also that of subsequent hardening. These properties make

this modification, like the hemihydrate, plaster of paris, practically important as estrich gypsum (flooring plaster). It is only capable of existence up to about  $600^{\circ}$ , and on heating above this temperature it turns into a third anhydrous modification  $\text{CaSO}_4\text{c}$ . This modification has lost all capacity for hydration and hardening, and is therefore a dead-burnt form which, however, differs from the dead-burnt form  $\text{CaSO}_4\text{a}$ , which is in unstable equilibrium from  $130^{\circ}$  to  $525^{\circ}$ , by the fact that the latter,  $\text{CaSO}_4\text{a}$ , can be given the capacity for hydration and hardening under certain conditions, while the former,  $\text{CaSO}_4\text{c}$ , cannot.

## 2. Plaster of Paris.

We have mentioned that when preparing the hemihydrate, plaster of paris, in practice by burning the dihydrate, a temperature is chosen which is fairly high above the transition point of the hemihydrate to the anhydrous form, mainly in order to attain sufficient velocity for the transformation, which theoretically should occur even at  $107^{\circ}$ . This temperature shows that at all events part of the hemihydrate must have been transformed into the anhydrous form. It is not completely transformed on calcining at a temperature not far from  $130^{\circ}$ , firstly, because the reaction-velocity for the transformation of the hemihydrate into the anhydrous form  $\text{CaSO}_4\text{a}$  is too small, just over the transition point. The second reason is the particular construction of the calcining apparatus. Köster\* states that in the rotating drum of the Petri-Hecking gypsum calcining apparatus the temperature is  $220^{\circ}$ , but owing to an ingenious mechanical contrivance the heat is rapidly removed from the gypsum above the transition temperature of  $130^{\circ}$ , and thus complete transformation into the anhydrous modification is hindered. The gypsum which is thus made in practice only consists to a small extent of the hemihydrate (plaster of paris), the greater part being the first anhydrous modification. Such gypsum can be employed technically, since the active mass need only be small, yet it must be in the finest possible state of division to possess the greatest possible reaction-velocity with water, so that in practice great stress is laid upon fineness of grinding. Such technically calcined gypsum forms an unstable system with water

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\* *Tonindustrie-Ztg.*, 1901, 32.

at ordinary temperatures, i.e. it will react by absorbing water. This process of absorption will require a certain time. Thus a paste of gypsum and water is first capable of being poured, after some time of being spread, and finally it becomes solid; after these stages, which are reached comparatively rapidly, the comparatively slow hardening takes place, i.e. an interlocking and felting of the gypsum crystals. From what we have already said on the phenomena of calcining gypsum, it is easy to see that different kinds of gypsum will be obtained, according to the different times and temperatures of calcination. The time during which the material can be poured or spread and is capable of setting varies with its composition, i.e. the hydration of the gypsum takes place at different velocities according to its content in hemihydrate. Moreover, a number of salts accelerate or retard the hydration to an extent proportional to their nature and concentration. Rohland considers this influence to be catalytic. Thus, samples of gypsum\* whose content in water of crystallisation only varied between 5 and 9 per cent showed variations of  $2\frac{1}{2}$  to 9 minutes in the time during which it was capable of being poured, and of 14 to 90 minutes in the setting-time. A knowledge of the catalytic action of added substances is of special interest in practice, since it is often important to be able to prolong at will the times for which the material can be poured or spread, and the setting-time. This can be effected by the action of negative catalytes for the reaction of hydration. (It may be added that these are really "false" catalytes, but for brevity we will simply speak of them as catalytes.) It may happen, owing to the presence of a positive catalyte, that the time of hydration is too small, i.e. the reaction of hydration takes place too fast, so that the material is of no practical use. This can be remedied by suitable negative catalytes. Interesting researches on the action of these catalytes have been made by Rohland, which have shown the reactions of hydration and hardening in a new light. He found that calcium chloride is indifferent, but that sodium chloride, lithium chloride, potassium dichromate, aluminium chloride and sulphate, potassium and sodium sulphate, accelerate the reaction of setting, while ferric chloride and two unspecified substances, A and B, retard it.

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\* *Ibid.*, 1901, 55.



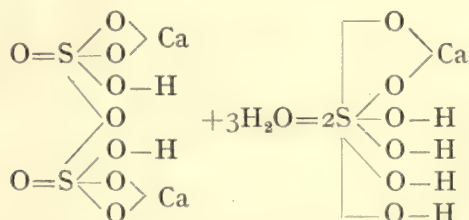
When two or more catalytes are present at once their action is sometimes additive, but sometimes the catalytes mutually weaken one another till in many cases they compensate one another ; in other cases, again, the action may be greater than the sum of their separate actions. The time which elapses between the beginning and the end of the setting (hydration) period is the greater the more negative is the catalyte, i.e. the stronger is its retarding tendency. This time is shorter the more positive is the catalyte, i.e. the greater is its acceleration of the hydration velocity. When the hydration period is short the added substances, whether accelerating or retarding, exert a greater action than when the period is long. On the other hand, the action of the added substances is weaker the greater is the content in combined water. When the calcium sulphate contains no water (dead-burnt gypsum) we have observed that the reaction-velocity is excessively small ; in this case added substances still exert an effect, though this is not so intense. As we have already said, the slowness of reaction of dead-burnt gypsum is due to the formation of unstable complex molecules ; this lowers the reaction-velocity, of the combination with water and the hardening, to a very small value. We may assume that a decomposition of complex into normal molecules, proceeding and advancing slowly, would occur by the action of water with the aid of a catalyte, and that these normal molecules would then undergo the reaction of hardening. With the catalytes mentioned above the action is generally greater the higher the concentration. However, there is only very approximate proportionality, and even then only when the concentration is not too high. When positive catalytes are present and the maximum velocity is attained it decreases with further additions, so that the catalyte finally becomes indifferent, and even retarding at its highest concentration. This maximum of the reaction-velocity and the reversal point of positive to negative catalytic action lies at various concentrations according to the nature of the catalyte. It has been found that all those substances which exert an accelerating action raise the solution pressure of gypsum against water, while retarding substances lower it,\* and therefore Rohland regards the cause of the accelerating or retarding action of salt

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\* Cameron and Seidell, *Jour. Phys. Chem.*, 1901, **5**, 556 and 643.



solutions on hydration as lying in their action of raising or lowering the solution pressure of the gypsum. Thus we must consider these substances, whose mode of action points to changes of energy, as false catalytes (cap. II, 2). However, we will call them simply catalytes, in the sense used by Rohland. The knowledge which we have obtained as to the changes in solubility of gypsum in these electrolytic salt solutions renders it possible for us to draw an approximately true picture of what takes place in hydration and hardening. Rohland considers that the reaction consists of more than a mere felting of the gypsum crystals and the formation by this means of an interconnected mass. From the above-mentioned facts we can draw the practically important conclusion that the solid hemihydrate of gypsum must first pass into solution before the reaction with water can occur. We may note further that increase in the solubility of the gypsum results in a higher velocity of hydration and vice versa, so that the general conclusion can be drawn that a solid hydrates more rapidly the greater is its solution pressure against water. The reaction which thus takes place in solution is exothermic. In the special case of the hemihydrate of gypsum, Zulkowski \* gives a clear picture of the reactions which take place in the solution. Zulkowski considers the hemihydrate to be the calcium salt of a ditetrahydroxyl-sulphuric acid which passes into the calcium salt of a hexahydroxyl-sulphuric acid, combining with three molecules of water, thus :—



According to the law of mass action the solubility of  $\text{CaSO}_4$  must be depressed by the addition of an electrolyte containing a common ion, such as sodium or potassium sulphate. Actually, however, the solubility is found to increase, which is to be ex-

\* *Baumaterialienkunde*, 1899, 21 and 22.

plained on the assumption of the formation of complex ions. When the solubility-product of the calcium salt of hexahydroxylsulphuric acid is overstepped, a separation of crystals occurs from the supersaturated solution, which is to be regarded as a secondary result. A period then follows which is best termed the hardening period, including a mutual growth and felting of the gypsum crystals. These latter phenomena are only accompaniments of the hardening process, the main cause of which is the formation of a dilute solid solution, namely, that of the water of crystallisation or of constitution in the calcium sulphate. During this period any remaining hemihydrate splits up into dihydrate and anhydrite.

### 3. Estrich Gypsum.

Estrich gypsum, obtained from the dead-burnt gypsum  $\text{CaSO}_4\text{a}$  by calcining at a rather high temperature, is of technical importance, owing to its special strength and resistance to weather. It can also be obtained spontaneously from  $\text{CaSO}_4\text{a}$ , on rather long keeping, i.e. the change takes place with a very much slower velocity at ordinary temperatures. This fact, with others, shows that the dead-burnt form  $\text{CaSO}_4\text{a}$  is unstable compared with estrich gypsum; the reaction is one which proceeds spontaneously. Accordingly the transformation can be accelerated by suitable catalytes, such as sulphites of ammonium sodium or potassium, or sodium or ammonium chloride, which will accelerate the velocity of hydration of  $\text{CaSO}_4\text{a}$ , which of itself is excessively small. The hydration of estrich gypsum the second anhydrous form  $\text{CaSO}_4\text{b}$ , is much smaller than that of plaster of paris. The velocity of hydration of estrich gypsum is also influenced by catalytes, though not necessarily in the same direction.

The following table shows the catalytic action of various substances on the velocity of hydration of the two modifications of gypsum and of the transformation of dead-burnt gypsum ( $\rightarrow$  accelerating,  $\leftarrow$  retarding, o no action, — not investigated).

|  | Plaster of<br>Paris<br>( $\text{CaSO}_4\frac{1}{2}\text{H}_2\text{O}$ ) | Estrich<br>Gypsum<br>( $\text{CaSO}_4\text{b}$ ) | Dead-Burnt<br>Gypsum<br>( $\text{CaSO}_4\text{a}$ ) |
|--|---|--|---|
| NaCl   | →   | →  | 0   |
| CaCl <sub>2</sub>                                    | 0   | ←  | ←   |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>      | →   | →  | →   |
| AlCl <sub>3</sub>                                    | →   | ←  | —   |
| K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>        | →   | ←  | →   |
| K <sub>2</sub> SO <sub>4</sub>                       | →   | →  | →   |
| Na <sub>2</sub> SO <sub>4</sub>                      | →   | →  | —   |
| MgCl <sub>2</sub>                                    | →   | ←  | ←   |
| NH <sub>4</sub> Cl                                   | →   | ←  | ←   |
| KNO <sub>3</sub>                                     | →   | →  | →   |
| Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10aq. | ←   | ←  | ←   |

The intensity of the action of catalytes is different in plaster of paris and estrich gypsum. In the latter case also Rohland explains the catalytic action of single catalytes, or of several such, by the change in the solution pressure of the second anhydrous modification in the solution of the electrolyte acting as catalyte. The solution pressure against water of the second anhydrous modification is naturally different from that of the hemihydrate, and these pressures change in different directions and amounts against salt solutions. In estrich gypsum also only a small amount appears to be active, i.e. to possess the capacity of hydration, while the main portion is inactive and plays somewhat the same part in hardening as sand does in other hydraulic binding agents. Thus the active mass perhaps consists of another anhydrous form discovered by van 't Hoff, which can be obtained even at 100° and is therefore also unstable. According to van 't Hoff, if one part of plaster of paris is allowed to stand with 10 to 20 parts of water for one hour with occasional shaking, the dihydrate can be obtained finely divided in needles by sucking off the water and drying.

If this form is heated for rather a long time, only at 100°, (about 24 to 48 hours) an anhydrous form is obtained which is not dead-burnt gypsum, but a particular modification of the anhydrous form possessing the power of absorbing water and thus becoming solid in a few minutes. This anhydrous form appears to be the active part of estrich gypsum. The high velocity of hydration of van 't Hoff's anhydrite will be retarded

by the presence of the dead modification of which estrich gypsum mainly consists; this is confirmed by observations on the solidification of plaster of paris.

#### 4. Dead-Burnt Gypsum.

We have mentioned that dead-burnt gypsum  $\text{CaSO}_4\text{a}$  is a particular allotropic modification of  $\text{CaSO}_4$ , which, though possessing the capability for hydration, has lost all capability for hardening and is thus of no practical use for pouring and moulding, which is why it is termed dead-burnt. Since the active mass need only be very small, a product which is useful in practice can be obtained by mixing it with a suitable amount of hemihydrate. The hydration of the dead-burnt form is effected by the same catalytes as that of plaster of paris and estrich gypsum. As the last table shows, some catalytes act as for plaster of paris and others as for estrich gypsum, with the exception of  $\text{NaCl}$ , which in this case has no action. This behaviour suggests that this anhydrous form, a, can be considered as a kind of transition stage between the hemihydrate and the second anhydrous modification  $\text{CaSO}_4\text{b}$ , estrich gypsum. Positive catalytes impart to dead-burnt gypsum the capability for hardening, and Rohland explains the accelerating and retarding action of these catalytes in the same way as for the other two modifications by their raising or lowering the solution pressure of the modification  $\text{CaSO}_4\text{a}$  in the solution of the catalyte. It should be noted that obviously this  $\text{CaSO}_4\text{a}$  has a different solubility from  $\text{CaSO}_4\text{b}$  and  $\text{CaSO}_4, \frac{1}{2}\text{H}_2\text{O}$ , which is influenced differently by electrolytes, except  $\text{NaCl}$ , which in this case has no action. Natural anhydrite differs again in properties from the modifications so far mentioned. It is closest to  $\text{CaSO}_4\text{a}$ , since its velocity of hydration can be accelerated by powerful positive catalytes such as  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , by which it may also be made to harden. The two other methods of imparting the capabilities for hydration and hardening to dead-burnt gypsum, i.e. rather long keeping, and heating to a high temperature, completely fail for anhydrite. The really dead-burnt gypsum  $\text{CaSO}_4\text{c}$  obtained by heating over  $600^\circ$  cannot be made to hydrate or harden either by the action of positive catalytes or by the two methods given above. The really dead-burnt gypsum, however, is a stage after which fairly considerable decomposition begins to take place.



### 5. The Processes of Hydration (Setting) and Hardening of Portland Cement.

Portland cement is often made by making an intimate mixture of the raw materials, lime and clay, into bricks, which are dried in air and then burnt in a furnace. A loss of  $\text{CO}_2$  takes place as in burning lime, a loss of water as in calcining gypsum, and there are usually molecular changes also. It is an important question whether in Portland cement the combined or uncombined calcium oxide gives rise to hydration (setting) and hardening. The early experiments attempted to decide this question by determining the "free lime" in the cement before hydration and after hardening. However, the methods employed were not reliable since, for example, when dissolving out the lime by a cane sugar solution (Rebuffat), combined as well as free lime can be dissolved, for calcium silicate is hydrolytically dissociated to a considerable extent (p. 89). Fresh lime must pass into solution owing to hydrolysis, when calcium hydroxide combines with cane sugar to form a saccharate. Rohland\* has shown that the uncombined calcium oxide or hydroxide is the cause of hydration and hardening. He found that in the hydration of pure calcium oxide a number of substances exerted a catalytically accelerating ( $\rightarrow$ ), retarding ( $\leftarrow$ ) or indifferent (o) action as shown in the following table:—

|  |  |                 |
|--|--|-----------------|
| $\text{Al}_2(\text{SO}_4)_3 \rightarrow$ | $\text{K}_2\text{Cr}_2\text{O}_7 \leftarrow$ | $\text{NaCl o}$ |
| $\text{AlCl}_3 \rightarrow$              | $\text{K}_2\text{CrO}_4 \leftarrow$          | $\text{LiCl o}$ |
| $\text{CaCl}_2 \rightarrow$              |  |                 |
| $\text{BaCl}_2 \rightarrow$              |  |                 |

When these substances are added in small amount to the water which acts upon Portland cement, they influence its velocity of hydration in precisely the same manner. The substances which are indifferent to  $\text{CaO}$  have no action on Portland cement, while the activity of positive and negative catalytes shows an analogy in the two reactions even as far as its extent. There is thus no doubt that the uncombined calcium oxide or hydroxide plays an important part in the hydration or hardening of cement. Another accelerator for the hydration of portland cement is potassium sulphide,  $\text{K}_2\text{S}$ , the strength of whose action is inter-

\* *Zeit. f. anorg. Chemie*, 1899, 21.

mediate between  $\text{AlCl}_3$ , the strongest, and  $\text{CaCl}_2$ , the weakest of the accelerators. Of the substances which retard the hydration, boric acid has the most, and  $\text{FeCl}_3$  the least powerful action, while potassium bichromate, mentioned in the above table, occupies an average position. Among difficultly soluble substances, lead chromate and calcium sulphate exert a retarding action. If sea water is used to set Portland cement, the total action of the salts contained in the water will result in more or less retardation, depending on the composition. The main retarding action is due to  $\text{CaCl}_2$  and  $\text{CaSO}_4$ , produced by the interaction of the  $\text{CaO}$  of the cement with the  $\text{MgCl}_2$  and  $\text{MgSO}_4$  of the sea water. The above-mentioned experiments of Rohland, which were all carried out under comparable conditions throw light on the different actions of various kinds of Portland cement, of which two can be distinguished:—

- (1) Quick-setting Portland cement in which the reaction-velocity of binding the water is great, and
- (2) Slow-setting cement in which the reaction-velocity is small.

The time and temperature of burning play a part in this connection, since, according to Büsing and Schumann,\* under-burnt cement usually sets faster than well-burnt cement. There are numerous exceptions to this rule, e.g. there are raw materials which even after the most thorough burning give cements which set so rapidly that they can hardly be worked with water, especially when fresh. Rohland's experiments show that this is to be ascribed to the catalytic action of certain substances which are present in cement to a larger or smaller extent. If the content in aluminium compounds preponderates the cement sets rapidly; if this is not the case the setting-time of the cement becomes longer, since the catalytic action is in general proportional to the amount of catalyte. A fairly high  $\text{CaSO}_4$  content also retards the setting-time (time of hydration), since Rohland has found that this substance will exert a retarding action itself or will oppose the accelerating action of any aluminium compounds which are present. Rohland found that for rather small additions the action of the catalyte is proportional to its amount. However, in most cases, as in the setting of gypsum, this only

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\* *Der Portlandzement u. seine Anwendung*, p. 14.

holds up to a definite concentration of the catalyte, above which the action is reversed. Thus 7 per cent of  $\text{AlCl}_3$  in the water no longer accelerates, but retards the hydration. When using concentrated solutions of aluminium chloride the setting-time slowly rises still more. Phenomena of this kind are important in connection with the "change in setting-time," which is often noticed in practice. Slow-setting cements turn into quick-setting cements on storage, and this takes place faster, the greater the fineness of division. The cause of this is to be sought in the formation of one or more catalytes. Portland cement is not a system which is at rest in stable equilibrium, but its constitution changes continuously owing to the reactions which proceed in it. These take place excessively slowly, giving one or more positive catalytes (soluble aluminium compounds and alkalis). Since the reactions are taking place between solid substances, they will proceed faster the more finely divided is the reaction mixture, i.e. the more finely ground. The initially small reaction-velocity is accelerated owing to the heat produced, which is maintained for a fairly long time in the interior of the mass when large quantities are stored at a time. The reaction-velocity is also raised by the pressure which prevails in the interior, since this brings the separate particles closer together.\* Thus it is not surprising that, as the amount of the catalyte formed may vary enormously with the external conditions, the setting-time will vary correspondingly; this readily explains the variability of different kinds of cement in this respect.

The fact that the setting-time can be changed artificially by suitable additions is an illustration which shows that this change is due to catalytic action. By the addition or formation of hardly 0.9 per cent of an aluminium compound the setting-time of a slow-setting cement falls from 307 to 87 minutes, so that it becomes a quick-setting cement. The setting-time of a slow-setting Portland cement was 220 minutes without a catalyte; the addition of 0.3 per cent of sodium carbonate diminished it to 65 minutes, 0.7 per cent to 15-16 minutes and 1 per cent to 5 minutes. However, the action of the catalyte was reversed when its content exceeded 1 per cent, e.g. the addition of 4 per

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\* Spring found (*Bull. Soc. Chim.*, 1886, **46**, 229) that the reaction-velocity between solid  $\text{BaCl}_2$  and solid  $\text{CaSO}_4$  was raised by pressure,



cent prolonged the setting-time again to about 85 minutes. In another Portland cement the setting-time was prolonged from 8 to 180 minutes by the addition of 2 to 3 per cent sodium carbonate, thus transforming a quick-setting into a slow-setting cement. In the case of gypsum we observed that two catalytes together could exert an accelerating action greater than the sum of their separate actions ; this phenomenon is also observed in the case of cement. The setting-time of a slow-setting cement was 415 minutes ; this was reduced to 137 minutes by the addition of about 1 per cent of a positive catalyte, aluminium chloride, and to 80 minutes by the addition of the same quantity of aluminium sulphate. If the action were simply additive the setting-time would be 59 minutes when using both substances. However, the total action is found to exceed this limit, as the setting-time is reduced to 35 minutes.

This phenomenon is still more marked when using aluminium chloride and sodium carbonate simultaneously. Using sodium carbonate alone, the setting-time was found to be 105 minutes. When aluminium chloride and sodium carbonate acted simultaneously the time of hydration was reduced to 5-6 minutes. On the other hand, sodium chloride acts as a retarding catalyte. Thus a quick-setting cement, with a setting-time of about 45 minutes, was changed by the action of about 4 per cent sodium chloride into a slower-setting cement with a setting-time of 50 minutes. These examples, given by Rohland, throw light on the practical examples we mentioned before. The most varied actions of the different kinds of cements are due to the accelerating or retarding action of one catalyte, or to the combined accelerating, retarding, or compensating action of two or more catalytes. What we said for gypsum holds for Portland cement as to the cause of the action of the catalytes. Substances which raise the solubility of the substance undergoing hydration (setting) accelerate the setting-time, while substances which diminish the solubility retard it. The most important of the substances which undergo hydration are uncombined calcium oxide or hydroxide, and further, calcium aluminate and calcium silicate. As in the case of gypsum, a hardening reaction follows the hydration or setting reaction, but Rohland considers that there is no sharp boundary between the end of one and the beginning of the other : indeed, the two periods are partially superimposed. This over-



lapping of the two reactions explains the fact that binding of water by free  $\text{CaO}$  can occur after the end of the setting-time, especially in Portland cements which contain uncombined calcium oxide in rather large amounts and of rather low density. Consequently an increase of volume and cracking (the "blowing" of Portland cement) take place; it should be noted that this is connected with the density of the calcium oxide, since on this depends the reaction-velocity of combination with water. It has been observed that after rather long storage in rather damp air of cement which has a tendency to blow, this tendency is lost. This can be interpreted as showing that the reaction-velocity with which  $\text{CO}_2$  is bound is accelerated by the presence of water vapour; in fact, water is known to act as a catalyte in many oxidations. There is a difference between the reactions of hydration and hardening with respect to the influence of temperature; the temperature-coefficient (cf. p. 163) of hydration is high, while that of hardening is low. Moreover, in different Portland cements hydration ceases after a relatively short time, but hardening may extend over months and years according to the constitution of the Portland cement. The time at which the reaction-velocity of hydration and hardening approaches zero is followed by a period of reaction, the end of which is difficult to determine, being the point of complete absence of reaction. Numerous theories have been proposed to explain the hardening process, e.g. Le Chatelier regards the splitting up of basic calcium silicate into calcium monosilicate and calcium hydrate as the fundamental reaction of hardening. Rohland considers it to be important for the explanation of hardening that calcium oxide acquires a higher density, and probably a higher molecular magnitude, the higher is the temperature and the longer is the time of calcination in the manufacture of the lime from calcium carbonate. The tendency of calcium oxide to react decreases with rising temperature of calcination.

Silicates show the opposite property, since their power of reaction increases with rising temperature of calcination. The silicate components of the naturally occurring pozzolanas are already in this state, ready for reaction. This must be borne in mind in considering the pyrochemical reactions which take place in the manufacture of Portland cement at about  $1400^\circ$ ; the extent of capacity for reaction which is attained here deter-

mines the hardening reaction which takes place later at ordinary temperatures.

The equation (cap. I, 8)

$$\frac{d\ln K}{dT} = -\frac{Q}{RT^2}$$

shows that as the temperature rises in the manufacture of Portland cement, endothermic compounds will be produced, i.e. those formed with absorption of heat. Thus at ordinary temperatures these compounds are in unstable equilibrium, and accordingly they react with a greater or less reaction-velocity, spontaneously, towards the stable position of equilibrium. Rohland considers it most likely that a dilute solid solution of free calcium oxide in the other constituents of Portland cement, like that of carbon in iron (cf. cap. V, 6), is formed at the sintering point of the raw material. Van 't Hoff\* ascribed an osmotic pressure to these substances present in solid solution, as he did to substances in liquid solution. This readily explains the comparatively small reaction-velocity of the calcium oxide in Portland cement with water compared to the instantaneous velocity of the absorption of water when slaking pure lime with water. Thus we are not dealing with a simple hydration of quicklime as such, but of its solid solution, so that the value of the reaction-velocity is usually small. On the other hand, the silicate components are transformed at the sintering point into a state in which they are capable of reaction, presumably owing to the complex molecules present at ordinary temperatures being split up. Biltz † observed the occurrence of such a dissociation at high temperatures in the case of arsenic trioxide, which is bimolecular at red heat and monomolecular at white heat. A very likely reaction to underlie the hardening of Portland cement would be one in which the free lime tended to reach a state of equilibrium with the silicate components which are capable of reacting. E. Leduc's ‡ practical experiments support this view. As a purely physical cause, the action of unequal pressure may perhaps also be mentioned as explaining hardening. Therefore, there must be present a definite amount of calcium hydroxide

\* *Zeitschr. f. physikal. Chemie*, 1890, 5, 322.

† *Ibid.*, 1896, 19, 385.

‡ *Mon. scient.*, 15, 11, 633-635.

in hydrated Portland cement so that this can reach the degree of solidity and the other properties which make it such a valuable hydraulic binding agent. As in the case of gypsum (cf. cap. VI, 2), it has been noted by Otto Klein and J. F. Peckhaus\* that those components which effect the hydration and hardening (the active mass) are only present in small quantities. The comparatively greater inactive mass plays the same part as the sand which is added to Portland cement to make it more weather-resistant. This is not the place to discuss the various theories on the constitution of Portland cement, since no one of them is sufficiently universally accepted. As Rohland remarks, we must admit that all that has been established is merely that a number of substances which are present in certain quantities and under certain conditions tend towards final chemical equilibrium. It is only conjectural what reactions, compounds, and separations occur.

#### 6. The Weathering of Clay.†

We saw in the last section how important a part was played by storage in the development of technically useful Portland cement, and that the object was to lower the setting velocity if this was too great. This goes hand-in-hand with a change in volume, beginning with a decrease and finally turning to an increase. This process of storage plays a certain part both in clay, in which, as well as oxidation, a loosening occurs, resulting in a capacity for being more easily worked, and also in kaolin, the plasticity of which is raised. The explanation of the process occurring in the storage of clay and kaolin, which we term weathering, is chiefly given by the experiments of Rohland and by the older experiments of Seger.‡ Rohland considers that the plasticity of a material is determined by the power of the substance, or of a certain part of it, to form colloidal solutions with water (cf. cap. II, 5). Clay and kaolin contain such colloids, some inorganic, and some organic. The particular combination of these substances dissolved in water (active mass) with the clay substance itself, aluminium silicate, which in its purest form has the composition  $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ , is to be considered

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\* *Jour. Soc. Chem. Ind.*, **19**, 644.

† P. Rohland, *Zeitschr. f. anorg. Chem.*, 1904, **41**, 325-336.

‡ *Tonindustrie-Zeitung*, 1891, **15**, 813.



the cause of plasticity. The ratio  $\frac{M}{N}$  of the inactive mass to the active mass in the clay expresses the degree of plasticity. The clay is made practically useful by coagulating the colloidal solution contained in the mass. Rohland investigated the influence of various added substances on the coagulation and on the occurrence of plasticity, and found that neutral salts behave quite indifferently, while hydrolytically dissociated salts containing H or OH ions in solution accelerate coagulation and the occurrence of plasticity. Acids and bases behave quite similarly.

We may say quite generally that the above processes are accelerated by the presence of H ions or of OH ions. This statement must be qualified a little, since there is an essential difference in one point between the action of OH ions and H ions. The coagulation of the colloidal solutions in porcelain paste effected by OH ions is only brief and transitory; on the addition of OH ions to clay paste it again passes after some time into the unplastic state which was described by Seger, while by the addition of H ions it remains plastic in the same condition. The quantitative relationships between the intensity of action of H and OH ions and their concentration may be summarised by saying that there is an approximate proportionality between the two. The quantitative relation between the action of OH ions and their concentration naturally only extends over the transitory phase of the coagulation. Since we are dealing here with substances which when added in small quantities change the velocity of spontaneously occurring processes, we may call them catalytes. Those which accelerate the coagulation of the colloiddally dissolved substances in the porcelain paste and thus accelerate the occurrence of plasticity, so that the condition attained is permanent, may be termed positive catalytes (H ions). Substances which only cause a transitory pectisation (OH ions) may be regarded as negative, i.e. they finally retard coagulation and the occurrence of plasticity. We have mentioned that a certain parallel exists between colloidal properties and plasticity. The solutions actually used in clay pastes are all colloids of high molecular weight, such as alumina, silicic acid, glue, dextrine, etc., and these colloidal solutions possess the property of coagulating to a considerable extent. Such sub-



stances, possessing the characteristic colloidal properties, are distinguished from crystalloids by possessing to a greater or less extent those properties which are bound up with the conception of plasticity ; in particular they can be moulded, and they shrink in drying.\* We know that the velocity of coagulation is measurable, and must increase with increasing content of colloids in the porcelain paste. By the addition of small quantities of foreign substances the coagulation can be accelerated (H ions) or retarded (OH ions). However, in the coagulation of the colloids in a porcelain paste we are not dealing with one substance, but with a whole series of inorganic or organic substances, such as alumina, silicic acid, and the added organic muddy substances.

Rohland's† experiments have shown that in entire absence of colloidal substances a state resembling unplasticity is brought about, while, vice versa, the degree of plasticity may be raised before weathering by artificial addition of colloids (dextrine, tannic acid, alumina, pasty starch). Although these additions do not fulfil the object desired in practice, namely to increase the plasticity and at the same time to decrease the shrinkage, yet it appears legitimate to conclude that the property of plasticity is mainly determined by the presence of such colloids. The occurrence in a porcelain paste of that sum of properties which we term plasticity is not possible without the previous existence or formation of colloidal substances. The combination of such coagulable colloids with the clay substance itself; the aluminium silicate, appears to Rohland to be the cause of the occurrence of plasticity, taking into consideration the reactions we have mentioned during weathering. The increase of plasticity during weathering can be thus explained :—

The porcelain clay ready for storage gives an alkaline reaction, since the water in contact with it contains OH ions. This arises from the lean material, mainly felspar, which is hydrolysed by water, and especially from one component, calcium silicate, which is dissociated into hydroxide and silicic acid. The second important point is the decomposition during storage of the organic components of the clay and of the well water used.

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\* *Zeitschr. f. anorg. Chem.*, loc. cit.

† *Tonindustrie-Zeitung*, 1903, **27**, 128. Spechsaal, *Zeitschr. f. Keram. Glas. u. verw. Ind.*, 1903, **36**, 47.

It is probable that we must ascribe to ferments the action which causes weathering.

Ferments (cf. cap. II, 6), on the one hand, belong to the class of colloids, but on the other hand they are known as catalytes of many physiological processes. The result of this bacteriological or fermenting action is that a transformation takes place of the OH ions into inactive water, leaving an excess of H ions. This introduces the factor which accelerates the coagulation of the colloiddally dissolved inorganic and organic substances, and accelerates the occurrence and the degree of plasticity.

## CHAPTER VII

### OTHER APPLICATIONS OF THE PHASE RULE—THE DISTRIBUTION LAW— ADSORPTION COMPOUNDS—RECIPROCAL PAIRS OF SALTS

#### 1. The Conditions of Equilibrium of Two Substances which are Incompletely Miscible in the Liquid State.

LET us consider a system of two liquids which are only partially miscible, in the range of concentration of immiscibility (CD, Figure 30). The system consists of vapour in equilibrium with two liquid phases; saturated solution of B in A and saturated solution of A in B. Therefore, according to the phase rule, as we have two components in three phases, the equilibrium is univariant, i.e. at any temperature there is a perfectly definite vapour pressure of the system and a definite composition of the two phases.

In the phase diagram, Figure 30, this region of immiscibility is shown by the dotted curve CFD. At a given temperature corresponding to the isotherm GH, the composition of the saturated solution of the substance A in the substance B is given

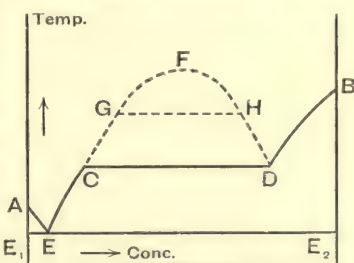


FIG. 30.

by the point H, and that of the saturated solution of B in A by the point G. We see that with rising temperature the mutual solubility of the two substances increases, as is usually the case, so that the range of immiscibility becomes smaller and smaller. At a definite temperature, the so-called critical solution point (F), a homogeneous solution results, i.e. the two liquids are completely miscible. On reducing the number of phases by one the system becomes bivariant.

Let us consider what happens when solid phases are present. Within the range of concentration BD, in which there is mis-

cibility of A and B, we have only one liquid phase together with the gaseous phase. If now the substance B separates out in the solid state we again obtain a univariant equilibrium; there is a definite concentration of the liquid phase for any given temperature. When the liquid phase has become poorer in B (i.e. richer in A) by the substance B crystallising out, a point is finally reached at which the solubility of A in B is overstepped, and the saturated solution of B in A results as a second liquid phase. This occurs at the concentration and temperature of the point D. Thus a new liquid phase has appeared in the system; there are now two components in four coexisting phases and the equilibrium is invariant. The result is that a further separation of B in the solid state must take place at constant temperature (or B may first separate out within the range CD). The separation of B causes no further change in concentration of the two liquid phases, and the only result is that the absolute quantity of the phase rich in B (which corresponds in composition to point D) steadily decreases, while the amount of the phase rich in A (which corresponds in composition to the point C) steadily increases. Finally, when the total concentration of the system (the sum of the two phases) corresponds to the point C, owing to the continual deposition of solid B at constant temperature, the phase rich in B (corresponding to the point D) is completely used up and the number of phases is reduced by one. The system is again univariant, i.e. separation of B occurs as in the range DB, on lowering the temperature. These conditions hold within the range CE until the concentration of the residual liquid corresponds to the eutectic point E, when the substance A in the solid state also separates out. The system again becomes invariant on the appearance of a new solid phase. E is therefore the eutectic point between B and A, and the meaning of the curve AE will be clear at once (cf. cap. V, 2); it represents the equilibrium of solid A with liquid. We may now set down the fields of existence of this system. They are:—

Above AECGFHDB. One liquid phase with gaseous phase.

Inside CGFHD. Two liquid phases with gaseous phase.

Inside AEE<sub>1</sub>. Solid A with one liquid and one gaseous phase.

Inside BDCEE<sub>2</sub>. Solid B with one liquid and one gaseous phase.

Below E<sub>1</sub>EE<sub>2</sub>. Solid A with solid B and gaseous phase.



## 2. Addition of a Third Substance to Two Incompletely Miscible Liquids. The Distribution Law.

Let us consider two incompletely miscible substances A and B, to which a third substance C is added at a given temperature. We will express the concentration of all possible mixtures of A and B by a straight line, the axis of abscissæ, the ends of which correspond to pure A and pure B. We will represent all ternary mixtures of A and B with C by using an equilateral triangle as suggested by Gibbs. Each angular point represents a pure substance (100 per cent), the three sides of the triangle represent the three possible binary systems AB, BC, CA, while all ternary mixtures lie within the area of the triangle (Figure 31).

To plot a ternary point or to find the composition corresponding to a given point P we make use of the property of an equilateral triangle that the sum of the parallels  $c$ ,  $b$ ,  $a$ , drawn from a point P to the three sides is equal to one side of the triangle, which represents 100 per cent of two substances. Thus if  $c$  is the percentage of the substance C, we cut off from AC the part  $AD=c$ , draw from D a line parallel to AB and cut off from this line a part  $b$ =percentage of B, and then draw parallels  $a$  and  $c$  to AC and BC, then the lines  $a$ ,  $b$ , and  $c$  represent the percentage of the substances A, B, and C in the ternary mixture. Their sum=one side of the triangle=100 per cent.

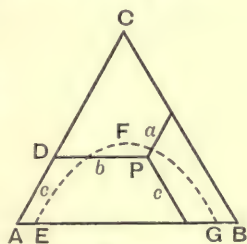


FIG. 31.

Now that we have considered the graphical meaning of the equilateral triangle we will examine the influence of the substance C on the binary partially miscible system AB. At the given temperature the range of immiscibility in the binary system AB is EG. Assuming that C is completely miscible with both A and B the solubility of the two substances A and B will increase as C is added. Thus the range of immiscibility will grow smaller and smaller with increasing additions of C, and will finally vanish at the point F when a definite amount of C has been added. Hence at a given temperature there are two distinct fields in the triangle:—

AEFGBC is the range of complete miscibility of the three substances and EFG is the range of incomplete miscibility.

Within the latter range there are two liquid phases of the substances A and B, consisting of saturated solution of A in B and saturated solution of B in A; C is shared between these two phases in a definite manner. Provided that C is only present in the system in small amount it will distribute itself between the two phases as a dilute solution. For fairly small additions of C this partition or distribution of C between the two liquid phases obeys the so-called Henry-Jungfleisch distribution law, which states that the ratio of the concentrations  $C_1$  and  $C_2$  of a substance distributed between two solvents, 1 and 2, is constant,

$$\frac{C_1}{C_2} = K.$$

If one of the substances is electrolytically dissociated the concentration always refers to the undissociated part. This law only holds in the above form when the distributed substance C has the same molecular weight in both liquid phases. If the molecular weight is  $n$  times as great in one solution, e.g. in 1, then the concentration of the substance C in solvent 1 appears in the equation as its  $n$ th root; thus,

$$\sqrt[n]{C_1} = K \text{ or } \frac{C_1}{C_2^n} = K_1,$$

and in this way the molecular weight of a substance in a given solvent can be determined by the distribution law. A third substance can be distributed not only between two liquids, but also between a liquid and a solid, by forming a dilute solid solution in the latter. In this case the distribution law holds for the solid-liquid system precisely as it did for the biphasic liquid system. There is an interesting application of this particular case in the theory of dyeing.

### 3. The Theory of Dyeing.\*

Substantive dyestuffs are acid dyestuffs with the specific property of dyeing cotton direct; they distribute themselves between the fibre and the dye bath in accordance with the distribution law (Witt).† The relation

\* Schwalbe, *Neue Färbetheorien*; Ahrens' Sammlung, 1908, XII, 113. Cf. especially the numerous researches of Suida, collected *Zeitschr. f. Farb. u. Textilchem.*, 1907, 6, 41.

† *Färberzeitung*, 1890-1, 1.

$$\frac{\sqrt{C_{\text{bath}}}}{C_{\text{fibre}}} = \text{const.}^*$$

has been found for dyeing silk with indigo-carmin in dilute solution, i.e. when dyeing light. According to the distribution law this means that the silk takes up the dyestuff in the form of single molecules, while in dilute dye baths double molecules are present, and still more complex molecules in concentrated

baths.† For dyeing with patent blue N,  $\frac{C_{\text{bath}}}{C_{\text{fibre}}} = \text{const.}$ , while

for cyanine,  $\frac{\sqrt{C_{\text{bath}}}}{C_{\text{fibre}}} = \text{const.}$  as before.

Witt suggests that adjective dyeing depends on the mordant present first being dissolved by the fibre and then keeping in solution by chemical action the dyestuff which diffuses into the fibre, thus causing an increase in the solubility of the dyestuff in the fibre. This simple theory of Witt has been modified by the most recent research, since it appears that dyeing depends more on adsorption phenomena than on the formation of dilute solid solutions. One of the facts supporting this view is that experiments in dyeing wool with picric acid gave a value of 2.7 for  $n$  in the equation

$$\frac{\sqrt[n]{C_{\text{bath}}}}{C_{\text{fibre}}} = \text{const.}^\ddagger$$

This would imply that picric acid has a molecular weight in aqueous solution 2.7 times greater than the simple molecular weight, although considering the electrolytic dissociation we should expect to find a smaller value in water than in silk. This result thus speaks against the theory of a dilute solid solution and in favour of that of an adsorption process. Adsorption phenomena have been minutely investigated by van Bemmelen.§

\* This value increases with rising concentration.

† Georgevics, *Monatsschr. f. Chem.*, **15**, 705-717; *Zeitschr. f. Färberei u. Textilindustrie*, 1901, 11.

‡ Walker and Appleyard, *Jour. Chem. Soc.*, 1896, **69**, 1334.

§ *Zeitschr. f. anorg. Chemie*, 1900, **23**, 321.

Adsorption really signifies that when a colloidal precipitate is brought in contact with a solution it takes up a certain part of it. The compound so produced is called an adsorption compound. Its composition depends on

- (1) The nature and structure of the adsorbing colloid.
- (2) The nature of the solvent.

The solvent power of the solvent for the adsorbed substance, on which the solubility depends, acts as a counter-force for the force of adsorption exerted on the dissolved substance by the colloid. Thus picric acid is more readily soluble in alcohol than in water, and it is taken up by silk fibres to a greater extent from aqueous than from alcoholic solution. If silk dyed with fuchsin is dipped into absolute alcohol this is coloured red, while the silk loses dyestuff; if the alcohol solution is diluted with water the dyestuff again goes to the silk. The fixation of the fuchsin on the fibre is determined solely by the concentration of the alcohol. The two solvents, dilute alcohol and the fibre, as it were, compete for the dyestuff, until after a certain time equilibrium sets in. Similar reactions occur in pure aqueous solutions when dyestuffs are employed which are not completely taken up by the fibre.

- (3) The nature and molecular condition of the substances dissolved in the solvent, e.g. whether they are present in a polymerised, molecular, ionised, or even colloidal state.
- (4) The temperature. In general the power of adsorption falls with rising temperature.\*

These points should make it clear that processes of adsorption obey laws similar to the distribution law.

The characteristic equation for adsorption is \*

$$\frac{x}{a} = Kc^m,$$

where  $x$  is the amount of the dissolved substance adsorbed,  $a$  the amount of the adsorbing substance, and  $c$  the concentration in the solution;  $K$  and  $m$  are constants.

When two colloids are in solution they may unite to yield an adsorption compound, and this reaction has an external analogy

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\* Freundlich and Losev, *Zeitschr. f. physik. Chemie*, 1907, **59**, 284.



with salt formation. Krafft\* has emphasised the colloidal nature of many dyestuffs, and Biltz† has succeeded in demonstrating the colloidal character of substantive and sulphur dyes, though a series of non-colloidal dyestuffs are known also.

Cross and Bevan,‡ Knecht,§ and Witt|| have shown that fibres without exception consist of substances belonging to the class of colloids. The two colloids, of which the dye is usually the positive and the fibre the negative, form an adsorption compound. In fact, Freundlich and Losev¶ observed a distribution of the dyestuffs crystal violet, crystal ponceau, new fuchsine, and patent blue between their aqueous solution and charcoal, or wool, silk, and cotton, according to exactly the same law. The following formula was deduced from their experiments:—

$$\lambda = \frac{v}{m} \ln \frac{a}{a-x} = a \left( \frac{a}{v} \right)^{-\frac{1}{n}}$$

in which  $v$  is the volume of the solution,  $m$  the amount of the adsorbing substance,  $a$  the amount of the dissolved substance capable of adsorption,  $x$  the amount adsorbed, and  $a$  and  $\frac{1}{n}$  constants. It should be noted that this formula of Freundlich and Losev is identical with the one given above, since by development as a series and neglecting the higher terms it is transformed into the form

$$\frac{x}{m} = ac^{\frac{1}{n}}.$$

In the case when the dyes are not colloidal, the colloidal precipitate of the fibre removes the dissolved crystalloidal substance from the solution with the formation of an adsorption compound. We can draw a distinction between crystalloidal and colloidal dyestuffs, for the former require fixation by special means, whereas the latter dye all fibres in one bath. There are transition substances, such as picric acid (see above) and methylene blue. As we have said, fixation must follow adsorption; the dyestuff only exists in the bath, and it is fixed on the fibre as an insoluble precipitate which is fast against washing. The colour may be formed by chemical precipitation, e.g. chrome-

\* *Chem. Ber.*, 1893, **32**, 1618.

† *Chem. Ber.*, **37**, 1766.

‡ *Researches*, 1906, **2**, 17.

§ *Zeitschr. f. Färberei u. Textilindustrie*, 1905, **4**, 139, 360.

|| *Chemische Technologie*, 1888, 369.

¶ *Loc. cit.*

yellow and indigo-blue ; it can also be formed by colloidal precipitation. This is the case in all direct substantive dyeing in the one-bath method, in which, therefore, the fixation spontaneously follows the adsorption. The fixation of many dyestuffs occurs by the colloidal solution coagulating, i.e. separating insoluble colloidal substances. The coagulation may take place spontaneously, but is usually catalytically accelerated by the structural elements of the fibre. The dye is formed in the bath and adheres to the walls of the vessel and to the fibre, which remains neutral in all cases. Therefore any dyestuff can dye any fibre, and the only question is whether the dye which results is of any use. Any soluble substance may serve as a dyestuff which can be transformed in suitable manner to an insoluble dye. In this sense mordanting is also a dyeing process,\* but the dye which is produced cannot be used, and dyeing is effected by improving the colour. Dyes and dyestuffs can be accurately distinguished, e.g. :—

| DYESTUFF              | DYE                     |
|-----------------------|-------------------------|
| Lead acetate          | Lead chromate           |
| Tannin                | Tannin-antimony-varnish |
| Aniline hydrochloride | Aniline-black           |
| Fuchsine              | Rosaniline base.        |

In the so-called acid and basic dyestuffs the dyes formed are free colloidal acids or bases. In direct cotton-dyeing the dyes which are formed are not chemically, but physically different. In general the two bodies cannot be transformed into one another by extraction with a solvent. They are only fast on washing when the dye has been produced by a thorough chemical change of the dyestuff. Colloidal coagulation is an example of such a change, since the coagulated substance can no longer be made soluble again to a marked extent by simple treatment with water.

In general we may say that in the dyeing of animal fibres adsorptive phenomena are accompanied and followed by chemical reactions, while in dyeing plant fibres the latter only play a subordinate part, if any.

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\* Zacharias, *Lehnes Färberzeitung*, 1901, 161-167.

#### 4. The Vulcanisation of Rubber.

The vulcanisation of rubber is a field which is extremely suitable for the application of the theory of adsorption compounds, as we see from the ingenious researches of F. W. Hinrichsen and his collaborators.\* Rubber occurs in the latex of certain species of plants. This latex is collected and rubber is separated in different ways, usually by heat or by the action of chemical reagents. As to the mechanism of this process C. O. Weber put forward the theory that the rubber is present in the latex as a hydrocarbon of low molecular weight, say  $C_{20}H_{32}$ , and that it is "polymerised" by coagulation and the subsequent mechanical treatment to the substance of high molecular weight, which forms the main constituent of the technical product.

Hinrichsen and Kindscher† shook out *Kickxia* latex with toluene in the cold and determined the depression of the freezing-point of the solvent, thus obtaining a value of 3000 for the molecular weight of the rubber. It undoubtedly follows from this observation that the rubber is present even in the latex as a typical colloid, and this is confirmed by the occurrence of Brownian motion observed ultra-microscopically in solutions of rubber in benzene.

The most important process in rubber manufacture is vulcanisation, which imparts to it those properties which are so valuable technically. The main, and almost the only theory of this process which prevailed was that of Weber, which, however, involved considerable difficulties. Cold vulcanisation is effected by treating the rubber at ordinary temperatures with a solution of sulphur chloride, e.g. in carbon bisulphide, and hot vulcanisation by treating with sulphur above the melting-point of sulphur. Weber assumed that the rubber formed a series of compounds with sulphur chloride or sulphur, e.g. in the former case lying between  $(C_{10}H_{16})_{10}, S_2Cl_2$  and  $(C_{10}H_{16})_{10}, (S_2Cl_2)_{10}$ . According to the more recent theories of colloidal chemistry it is more probable that adsorption processes come into consideration first in the action of sulphur chloride or sulphur on rubber. To decide the question whether chemical compounds or adsorption com-

\* Hinrichsen, *Zeitschr. f. Chemie u. Ind. d. Kolloide*, 1910, **7**, 65 and 202; *Zeitschr. f. angew. Chemie*, 1910, **23**, 1345 et seq.; *Chemiker-Ztg.*, 1909, 736 and 756.

† *Ber.*, 1909, **42**, 4329.



pounds were produced Hinrichsen and Kindscher first investigated the equilibrium between rubber and sulphur chloride in benzene solution. It was not possible to analyse the addition-product direct, and the only method of following the reaction was that of indirect analysis, which is often used in colloidal chemistry. The rubber solution was treated with the sulphur chloride solution and the resulting precipitate allowed to settle. Part of the clear supernatant solution was pipetted off and the content in free sulphur chloride determined. Knowing the total volume of the liquid, the amount of combined sulphur chloride could be calculated. If the amount of sulphur chloride consumed is plotted against the amount originally taken, the shape of the curve so obtained will enable us to decide whether a chemical or adsorption compound is present. In the latter case the equation is

$$\frac{x}{a} = K.c^m,$$

where  $x$  is the sulphur chloride consumed,  $a$  the concentration of rubber,  $c$  the initial concentration of sulphur chloride, and  $K$  and  $m$  constants. In this way continuous curves are obtained which start at zero and rise first rapidly, then more slowly, and finally asymptotically parallel to the axis of abscissæ. If, on the other hand, there is a chemical compound, the consumption of sulphur chloride must be constant within the range of the stability of that stage of combination. The following results were obtained with 0.5 gram. rubber and different amounts of  $S_2Cl_2$ , taking special precautions (careful exclusion of atmospheric moisture):—

| Grms. $S_2Cl_2$ taken | Grms. $S_2Cl_2$ used | Grms. $S_2Cl_2$ taken | Grms. $S_2Cl_2$ used |
|-----------------------|----------------------|-----------------------|----------------------|
| 0.4330                | 0.2552               | 1.0825                | 0.2795               |
| 0.4330                | 0.2526               | 1.0825                | 0.2685               |
| 0.6495                | 0.2679               | 1.0825                | 0.2740               |
| 0.6495                | 0.2535               | 1.2990                | 0.2644               |

We see from this table that the sulphur chloride consumed by the same amount of rubber is approximately constant and independent of the excess of sulphur chloride which was taken. This interesting fact indicates that the precipitate actually contains



a definite chemical compound. The groups  $C_{10}H_{16}$  and  $S_2Cl_2$  have approximately the same molecular weight (136 and 135), so that a consumption of 0.25 gm. sulphur chloride by 0.5 gm. rubber corresponds to a compound of the composition  $(C_{10}H_{16})_2, S_2Cl_2$ . These experiments certainly prove that we must allow for the formation of a definite compound between sulphur chloride and rubber in cold vulcanisation just as we do in the formation of tetrabromide by the action of bromine. No evidence was found for the presence of other stages of combination as assumed by Weber.

It should be specially noted that the proof of the existence of a definite chemical compound by no means excludes the possibility of adsorption phenomena playing an important part in cold vulcanisation. The experiments of Hinrichsen and his collaborators were performed in solution carefully excluding traces of moisture, but excess of atmospheric moisture renders possible the separation of sulphur from sulphur chloride, and thus a production of adsorption compounds. Commercial cold vulcanised rubber goods are thus best considered as showing adsorption of sulphur in "solid" or "semi-solid" solution in the sulphur chloride addition-product in excess of the rubber.

In order to study hot vulcanisation, E. Stern\* investigated the equilibrium between rubber and sulphur at a high temperature, using naphthalene as solvent. Molten naphthalene dissolves sulphur in considerable amount and also possesses marked swelling- or solvent-power for rubber. A homogeneous system is obtained by using a solvent, and this avoids difficulties arising out of the condition and previous treatment of the rubber. A rubber-sulphur naphthalene solution was kept heated in a thermostat, and samples were removed with suitable precautions after various times. The rubber was extracted with acetone, and when the free sulphur was completely removed by this means, the sample was dried and its content in combined sulphur was determined. The following table shows the result of changing the concentration of sulphur, the time being the same in each case :—

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\* *Chemiker-Ztg.*, 1909, 756.

| Rubber solution<br>in grms.<br>(90 grms. naphtha-<br>lene, 5 grms. Para*) | S<br>in grms. | Ratio of<br>concentration | Grm. BaSO <sub>4</sub> found<br>per grm. vulcanised<br>rubber (1 hour<br>at 150°) |
|---|---------------|---------------------------|---|
| 18.66   | 1.178         | 95 : 6 (1)                | 0.278 (1)   |
| 23.15   | 2.193         | 95 : 9 (1.5)              | 0.467 (1.7)   |
| 23.06   | 2.912         | 96 : 12 (2)               | 0.564 (2)   |

This shows that when the time is constant the sulphur consumed is proportional to the sulphur taken, which, as Wo Ostwald† has shown, points to pure adsorption compounds in hot vulcanisation. The following table shows the influence of time on vulcanisation, taking 5.07 grms. Para in 90 grms. naphthalene with 6 grms. S at 150° :—

| Time             | Grms. rubber<br>(vulcanised) | Grm. BaSO <sub>4</sub> | % S. |
|------------------|------------------------------|------------------------|------|
| 10 <sup>08</sup> | —                            | —                      | —    |
| 11 <sup>21</sup> | 0.6689                       | 0.138                  | 2.8  |
| 12 <sup>17</sup> | 0.5496                       | 0.183                  | 4.7  |
| 1 <sup>30</sup>  | 0.7762                       | 0.497                  | 8.9  |
| 2 <sup>26</sup>  | 0.5784                       | 0.412                  | 10.0 |

If we regard vulcanisation from the standpoint of the principles of equilibrium, we are led to believe that the reaction between rubber and sulphur must occur even at temperatures below the melting-point of sulphur, though with a smaller reaction velocity. In fact, duration experiments (A. Martens) show that the reaction occurs perceptibly even at about 70° after some days. On the other hand, it seems likely that under certain conditions it should be possible to reverse the reaction, i.e. remove the combined sulphur from the vulcanised rubber. Research on these lines may prove important in the theory of reclaiming old rubber.

### 5. The Manufacture of Soap.‡

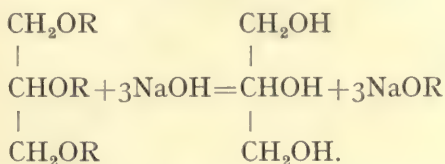
The behaviour of systems with two liquid layers is, as we shall now see, of particular importance for the theory of the manufacture of soap. The operations which take place are briefly the

\* Para rubber.

† *Zeitschr. f. Chemie u. Ind. d. Kolloide*, 1910, **6**, 136.

‡ Merklen, *Zur Theorie der Kernseifen*, pub. Knapp.

following : The fats or oils used in the manufacture of soap are triglycerides, the glycerol esters of fatty acids ; they are first saponified :—



(R is the fatty acid radical.) This would appear to be a quadrimolecular reaction, but experiment has shown that there are three stages of the reaction which proceed simultaneously, and are bimolecular ; the first product is diglyceride, the next monoglyceride, and finally free glycerol is obtained by the last of these reactions. The reaction-velocities of the three partial reactions are in the ratio 1 : 2 : 3, which causes the total reaction to appear as if it were bimolecular ;\* this has been observed experimentally.† The sodium salts of the fatty acids which result from the saponification are soaps. These are then separated from their solution or, as it is termed, “ salted out ” or “ grained ” by the action of an inorganic sodium salt. The reason for the separation of the soap from the solution can be easily understood from the law of mass action. The dissociation of soap, which is the sodium salt of a comparatively weak fatty acid, is depressed by the action of a common ion, i.e. the solubility-product is overstepped and solid soap separates out, called “ curd.” The aqueous layer below is drawn off and an alkaline lye containing salt is added. This is boiled and an equilibrium reached between the lye and the pasty mass of soap. The concentration of the lye is then gradually reduced by dilution with water, when the mass boils.

After each addition of water a fresh equilibrium sets in, till finally a concentration is reached, characteristic for each soap, at which the soap begins to dissolve. We may call the concentration of the lye at this point the limiting concentration of the solubility of the soap. The more water is now added the more soap dissolves. Together with this there is a transformation of the soap which at first was in equilibrium with the original lye

\* Abel, *Z. f. Elektroch.*, 1906, **12**, 681. *Zeitschr. f. physikal. Chemie*, **56**, 558.

† Kremann, *Monatsh. f. Chemie*, 1906, **27**, 1607.

in the form of small unconnected granular clumps. As the lye becomes dilute these swell up more and more, the surfaces of separation become less sharp, and finally a single connected mass is obtained. When this point is reached the operation is over, the boiling is stopped and the kettle is allowed to cool. The system is now apparently biphasic; the upper layer is a commercial product, curd soap, consisting as we shall see of an adsorption compound of the colloidal soap and of alkaline lye containing salt; the lower layer is the colloidal solution of soap in an alkaline lye containing salt. The colloidal nature of soap in its solution was deduced by Krafft mainly from the fact that the boiling-point of a pure soap solution is practically the same as that of water (cf. cap. II, 5). Let us consider the above system from the standpoint of the phase rule. The components are soap, water, NaOH, NaCl, and glycerol. Beyond the gaseous phase there are obviously two phases, consisting of curd soap and the lye; but each of these phases is a colloidal solution, i.e. biphasic, so that in the whole system we may almost say that there are five phases. Applying the phase rule we find that the equilibrium is bivariant, i.e. there can be different equilibria at any temperature according to the concentration of the components. Remembering that in practice  $\text{Na}_2\text{CO}_3$  may also be present in solution, which increases the number of components by one, we see that the curd soap of commerce is bound to be a product whose composition and properties are not fixed, and, in fact, may undergo considerable variations. At the boiling-point, both of the phases, that rich in soap and that poor in soap, are colloidal solutions. In these colloidal solutions the colloidal particles interact with the alkaline salt solutions, which we may call the continuous phase, in the manner we have already discussed on page 176, and the separate particles form adsorption compounds whose composition depends on that of the continuous phase. They are in equilibrium with the continuous phase at each temperature, initially at the boiling temperature. As the temperature falls the equilibrium shifts by more of one of the phases being formed. Thus the two colloidal phases, curd and lye, pass through a series of equilibria as the temperature falls. This phenomenon can be readily observed in the lye at once, since in this case the liquid is the greater component, but in the curd soap it is only noticed after slow cooling as crystalline streaks



or veins, which usually radiate from centres. This is termed "figging" by the soap boiler. Practical advantage is taken of this behaviour in the manufacture of the so-called mottled Marseilles soap. When making this soap it is preferred to conduct the boiling purposely so as to facilitate the production of separate phases on cooling. The chief condition for this is that the soap shall contain a comparatively large amount of water and electrolyte. The separation can be rendered visible by the addition of an insoluble powder, e.g. of ferric oxide, which otherwise behaves passively. The part which separates out, richer in soap, is white, while the residual continuous phase, which is poorer in soap, holds the ferric oxide in suspension and thus appears red. This separation in the curd takes place in a colloidal mass which is only semi-fluid and hence the two layers are not sharply separated, but the two solutions run into one another and thus form the mottling. We have already discussed the importance of hydrolysis in the manufacture of soap (cf. cap. III, 5).

#### 6. The Parkes Process.

This process is for the treatment of lead poor in silver by adding certain quantities of zinc to the molten metal heated above the melting-point of zinc. Zinc and lead only dissolve one another very incompletely in the liquid state; the range of immiscibility extends from

|    |                          |
|----|--------------------------|
|    | 0.5 % lead (99.5 % zinc) |
| to | 98.5 % „ (1.5 % „ ).     |

The silver which is present in small quantities distributes itself between the two solvents, lead and zinc, so that in the liquid state practically all the silver is dissolved in the zinc and only very small quantities in the lead. On cooling, mixed crystals of silver and zinc separate out from the upper zinc-silver layer, and these crystals are then removed by skimming off.

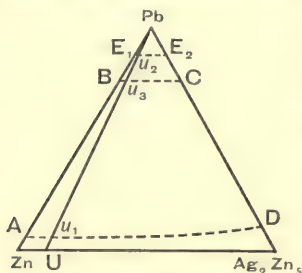
To understand the theory of this process we require a knowledge of the ternary system  $\text{Ag-Zn-Pb}$ .

Obviously it is only the mixtures poor in silver which are of technical interest, so that we shall confine ourselves to this portion of the ternary system. Silver and zinc form the compounds  $\text{Ag}_3\text{Zn}_2$ ,  $\text{AgZn}$ ,  $\text{Ag}_2\text{Zn}_3$ , and  $\text{Ag}_2\text{Zn}_5$ , so that the whole

ternary system Ag—Zn—Pb is made up of the following five ternary partial systems :—

- (1) Ag—Ag<sub>3</sub>Zn<sub>2</sub>—Pb
- (2) Ag<sub>3</sub>Zn<sub>2</sub>—AgZn—Pb
- (3) AgZn—Ag<sub>2</sub>Zn<sub>3</sub>—Pb
- (4) Ag<sub>2</sub>Zn<sub>3</sub>—Ag<sub>2</sub>Zn<sub>5</sub>—Pb
- (5) Ag<sub>2</sub>Zn<sub>5</sub>—Zn—Pb

It is only the system poorest in silver, i.e. Ag<sub>2</sub>Zn<sub>5</sub>—Zn—Pb, which is important in the Parkes process, and we shall now examine the conditions of equilibrium in this system. We may represent the concentrations graphically by the use of an equilateral triangle (cf. cap. VII, 2), and we will set out the corresponding solid-liquid equilibrium temperatures as perpendiculars to the concentrations in question. A plane projection of this space diagram corresponds to the equilateral triangle and



temperatures cannot be seen on it. To show the different fields more plainly, the figure is diagrammatic. However, we will give important fixed points numerically in the text.

We have mentioned that the binary system, Zn—Pb, shows a gap\* in the miscibility from 0.5 to 98.5 per cent Pb. The binary system Pb—Ag<sub>2</sub>Zn<sub>5</sub> also shows a gap† from about 1 to 98 per cent Pb. The third binary system, Zn—Ag<sub>2</sub>Zn<sub>5</sub>, gives isomorphous mixtures of Roozeboom's Type 4 with a transition point U. Thus there are the following fields in the ternary system :—

Field AU<sub>1</sub>UZn, in which the mixed crystals rich in zinc first separate out from the homogeneous phase rich in zinc. Mixtures within this range of concentration pass into the field AU<sub>1</sub>U<sub>3</sub>Pb on crystallisation, after sufficient zinc has separated out in the form of an isomorphous mixture, Ag<sub>2</sub>Zn<sub>5</sub>—Zn. In this field there is a biphasic system consisting of a layer rich in zinc and one rich in lead; the silver is distributed between these layers so that most of it is in the zinc layer. Within this range of concen

\* Spring, *Zeitschr. f. anorgan. Chemie.*

† F. Hofmeier, *Dissertation*, Graz, 1910.

tration, mixed crystals  $\text{Ag}_2\text{Zn}_5$ —Zn rich in zinc first separate out from the layer rich in zinc. Finally the phase rich in zinc disappears and we pass into the field  $\text{E}_1\text{U}_3\text{U}_2\text{B}$ . Crystallisation of the isomorphous mixed crystals  $\text{Ag}_2\text{Zn}_5$ —Zn takes place from the lead phase till we reach the eutectic curve  $\text{E}_1\text{U}_2$ , at which lead separates out simultaneously as the temperature falls, till the mass is all solid. Similar changes take place with respect to the mixed crystals of  $\text{Ag}_2\text{Zn}_5$ —Zn (which are rich in  $\text{Ag}_2\text{Zn}_5$ ) within the field  $\text{UU}_1\text{Ag}_2\text{Zn}_5\text{D}$  (homogeneous phase rich in zinc), within the fields  $\text{U}_1\text{DCU}_3$  (biphasic system: phases rich in zinc and in lead) and  $\text{U}_3\text{U}_2\text{E}_2\text{C}$  (one phase rich in lead). In the limiting case, if during crystallisation the residual melt reaches the concentration corresponding to  $\text{UU}_1\text{U}_3\text{U}_2$ , then the crystallisation takes place along this line until the composition of the point  $\text{U}_2$  has been reached; this point already belongs to the eutectic curve  $\text{E}_1\text{U}_2\text{E}_2$ . In the field  $\text{PbE}_1\text{U}_2\text{E}_2$  lead separates out first, as the temperature falls, till the melt has the composition of points on the eutectic curve  $\text{E}_1\text{U}_2\text{E}_2$ . Mixed crystals rich or poor in zinc separate out as the temperature falls further, together with solid lead. The eutectic curves  $\text{E}_1\text{U}_2$  and  $\text{U}_2\text{E}_2$  do not correspond to homogeneous freezing at a definite temperature, since we can see from the phase rule that the equilibrium is univariant, as there are three components in only four phases, one liquid, two solid (Pb and one kind of mixed crystals), and one gaseous phase. The equilibrium is only invariant at the point  $\text{U}_2$  (beyond the points  $\text{E}_1$  and  $\text{E}_2$ ), where there is one liquid and one gaseous phase coexisting with three solid phases, lead and the two kinds of mixed crystals; thus the temperature at  $\text{U}_2$  is absolutely fixed. The temperatures of  $\text{E}_1$ ,  $\text{U}_2$ , and  $\text{E}_2$  are very close together, near  $300^\circ$ , and thus they can only be found experimentally with difficulty.

In actual practice in the Parkes process the argentiferous lead is heated above the melting-point of zinc, and 1.3 to 2.3 per cent of zinc is added in portions according to the silver content 0.14 to 0.44 per cent. It should be noted that the lead usually contains copper and gold and other impurities, in the case of American ores to a considerable extent, so that in this case the lead is first refined in special furnaces. If gold and copper, and in some cases nickel, are to be separated, only a very small part of the whole amount of zinc is added at first, when the so-called copper scum



separates out. If the treatment is only for the recovery of silver, about two-thirds of the zinc is added at first, i.e. 0.86 to 1.54 per cent. The melted metal of such a composition is now cooled nearly to the point at which lead crystals are formed. Owing to the low specific gravity the crystals of the zinc-silver alloy, which may contain copper and gold in some cases, move upwards, when they are skimmed off with a sieve-like iron ladle. The vessel is again heated and the operation repeated with a third and fourth quite small addition of zinc. The zinc-silver alloy, with which a considerable amount of lead is still mechanically admixed, is called briefly zinc scum. Refined lead is left behind.

Let us consider this process in the light of the researches of R. Kremann and F. Hofmeier on the ternary system Ag—Pb—

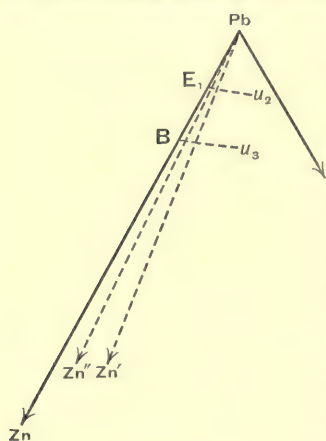


FIG. 33.

Zn. The metal employed in practice has a low silver content and thus lies within the range of concentration very near the side PbZn (corresponding to the binary system Pb—Zn), say on the line PbZn' (Figure 33). Kremann and Hofmeier give a content of 99 to 100 per cent Pb (say 99.5 per cent!) for the composition of the eutectic binary point of a mixture of lead and zinc containing 1 per cent of silver. The eutectic point between pure lead and zinc should lie at the same composition, and thus the binary eutectic curve be-

tween lead and the isomorphous mixed crystals  $\text{Zn—Zn}_5\text{Ag}_2$  lies at a concentration of 99.5 per cent Pb. In practice the addition of zinc has always to be adjusted (0.8 to 1.5) to bring the system outside the lead field, and therefore mixed crystals  $\text{Zn—Ag}_2\text{Zn}_5$  crystallise out first. After some time, owing to the separation of these crystals, the system reaches the binary eutectic curve  $E_1U_2$  between Pb and the mixed crystals rich in Zn, i.e. it deposits pure lead at the same time as the mixed crystals  $\text{Ag}_2\text{Zn}_5\text{—Zn}$  rich in zinc. Technical results show that zinc scum contains relatively much lead, so that presumably the system moves to a certain extent on to this binary eutectic curve. The crystals which have separated are



then removed and the mother-liquor is remelted with a fresh amount of zinc; it contains an amount of silver proportional to the amount of the ternary eutectic mixture. After the second addition of zinc the concentration lies still closer to the binary system PbZn, say on the line PbZn", since the melt becomes poorer in silver owing to the first removal of crystals. Each further operation brings us closer to PbZn, thus still further reducing the absolute quantity of the ternary eutectic (with pure lead=0), so that the amount of silver remaining in the lead must become smaller and smaller by repetition of the operation of adding zinc and removing the ZnAg crystals. The best technical results give a content of 0.0005 per cent Ag in the residual lead; it is obvious that a theoretically complete removal of silver is impossible. We should note that in actual practice we rarely pass into the field of two liquid layers, since this is over 1.5 per cent of zinc and less is usually added. The zinc scum is further treated by segregation, i.e. heated to a rather high temperature, when the ternary eutectic melts first, consisting of mixed crystals of Pb and Zn-Ag<sub>2</sub>Zn<sub>5</sub>. During this process, as the temperature rises we move on to the eutectic curve E<sub>1</sub>U<sub>2</sub> between Pb and mixed crystals of Zn-Ag<sub>2</sub>Zn<sub>5</sub>, till finally the whole of the lead is liquid, and only zinc-silver crystals are left.

#### 7. Reciprocal Pairs of Salts. The Ammonia-Soda Process, from the Standpoint of the Phase Rule.\*

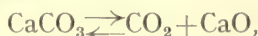
In 1902, 1,760,000 tons of soda were produced, of which only 150,000 tons were made by the old Le Blanc process. Soda is now chiefly produced by the ammonia-soda (Solvay) process. This process consists in carbonating brine saturated with ammonia by means of carbon dioxide, and to understand its theory we ought not to consider it apart from its actual working in practice. The basis of the process is a simple double decomposition.



This is a case of the so-called reciprocal pairs of salts. It depends on the conditions whether the reaction goes from right to left or from left to right. We have already considered similar double decompositions in Chapter III when dealing with caustifi-

\* Fedotieff, *Zeitschr. f. phys. Chem.*, **49**, 162.

cation. In the latter case we were concerned with the reactions in the solution, i.e. the homogeneous system, so that we were able to obtain a theoretical basis for technical working by the application of the law of mass action alone. In the present case we are also concerned with the amount and nature of the solid phase, as when we were discussing the loss of soda in caustification, so that we must now use the phase rule as a guide. The ammonia-soda reaction is a case of the equilibrium of four components, and is thus very complicated from the point of view of the phase rule. We must first emphasise the fact that the salts in question are not four independent components, but only three, as the fourth can always be expressed in terms of the other three. This recalls the reaction



in which there were two, not three, independent components. In the present case, when the equilibrium is univariant, three components must be present in the solid phase, since there are four components (water and three salts) in five phases (three solid phases, solution and vapour). It is only in this case that there is a fixed composition of the solution at every temperature.

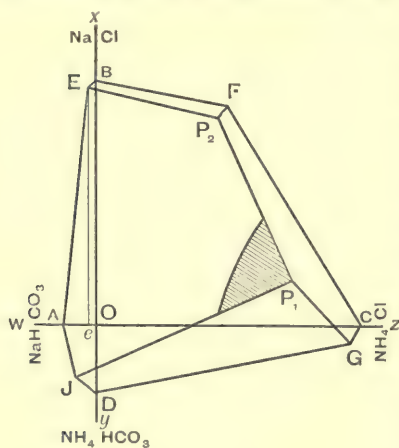


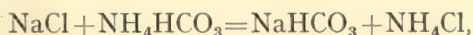
FIG. 34.

In the experiments of Fedotieff to explain the ammonia-soda process the solutions used were always saturated with  $\text{CO}_2$ . It might be said that  $\text{CO}_2$  ought to be considered another independent component from the point of view of the phase rule. Yet it is not an independent variable, since the solutions were always saturated with  $\text{CO}_2$  and therefore  $p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 1 \text{ atm}$ .

The partial pressure of the water depends on the composition of the solution, and this equation

shows that the same holds for the carbon dioxide. Thus it is not an independent component: the number of substances has, indeed, been increased by one, but the number of equations governing the process has also been increased by one, at the

same time. One of the most important points in experiments of this kind is the method of representing the results graphically. In the case of reciprocal pairs of salts, besides the elegant new method of Jännecke, we may use a system of co-ordinates in space, with four axes drawn like sides of a regular octahedron meeting at a point O. The adjacent axes are at an angle of  $60^\circ$  and the opposite axes at  $90^\circ$ . To represent graphically the reaction



we plot the solubility of each salt on each axis in suitable units (e.g. moles per lit.  $\text{H}_2\text{O}$ ). Salts with common ions are plotted on adjacent axes. Excluding the formation of complex or double salts, the solubility of a salt is in general lowered by the addition of a salt with a common ion, in accordance with the law of mass action. The concentrations of solutions containing two salts with a common ion lie on the surfaces of the octahedron. In this way curves are obtained representing changes in the solubility of each salt on addition of the second salt, and the point at which two such curves intersect represents saturation of both salts. Solutions containing all three salts lie within the space enclosed by the four surfaces of the octahedron. For our purpose we will use a special form of projection of this space diagram; we thus obtain for our system of co-ordinates two straight lines,  $xy$  and  $wz$ , intersecting at right angles. We mark out on the four lines,  $Ox$ ,  $Oy$ ,  $Ow$ , and  $Oz$  (Figure 34), the solubility of the pure salts which take part in the ammonia-soda process\* :—

| Saturated with<br>pure           | Line | Solubility in<br>1 litre water† |
|----------------------------------|------|---------------------------------|
| $\text{NaCl}$ . . . . .          | OB   | 6.09                            |
| $\text{NaHCO}_3$ . . . .         | OA   | 0.82                            |
| $\text{NH}_4\text{HCO}_3$ . . .  | OD   | 1.52                            |
| $\text{NH}_4\text{Cl}$ . . . . . | OC   | 5.57                            |

Points corresponding to two salts, e.g. E which represents

\* The unit of measurement is  $\frac{1}{\sqrt{2}}$  less than that in space. Cf. R. Kremann, *Leitfaden der graphischen Chemie*, pub. Bornträger, 1910.

† Unless stated to the contrary, the data given in this and following table relate to  $0^\circ$ .

saturation with NaCl and  $\text{NaHCO}_3$ , are constructed by marking off the content in  $\text{NaHCO}_3$  on its axis as Oe, and marking off the content of NaCl on a perpendicular drawn from e. The following table gives the solubility of the four solutions each saturated with a pair of salts having a common ion, and the meaning of the lines in Figure 34 :—

| Saturated with  | Line or Point | Solubility L. of       |                           |
|---|---------------|------------------------|---------------------------|
| NaCl with addition of $\text{NaHCO}_3$ . . .                            | E B           | —                      | —                         |
| NaCl " " " $\text{NH}_4\text{Cl}$ . . .                                 | B F           | $\text{NH}_4\text{Cl}$ | NaCl                      |
| NaCl and $\text{NH}_4\text{Cl}$ . . .                                   | F             | 2.73                   | 4.89                      |
| $\text{NH}_4\text{Cl}$ with addition of NaCl . . .                      | F C           | —                      | —                         |
| $\text{NH}_4\text{Cl}$ " " " $\text{NH}_4\text{HCO}_3$ . . .            | C G           | $\text{NH}_4\text{Cl}$ | $\text{NH}_4\text{HCO}_3$ |
| $\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{HCO}_3$ . . .              | G             | 5.42                   | 0.46                      |
| $\text{NH}_4\text{HCO}_3$ with addition of $\text{NH}_4\text{Cl}$ . . . | G D           | —                      | —                         |
| $\text{NH}_4\text{HCO}_3$ " " " $\text{NaHCO}_3$ . . .                  | D J           | $\text{NaHCO}_3$       | $\text{NH}_4\text{HCO}_3$ |
| $\text{NH}_4\text{HCO}_3$ and $\text{NaHCO}_3$ . . .                    | J             | 0.58                   | 1.39                      |
| $\text{NaHCO}_3$ with addition of $\text{NH}_4\text{HCO}_3$ . . .       | J A           | —                      | —                         |
| $\text{NaHCO}_3$ " " " NaCl . . .                                       | A E           | $\text{NaHCO}_3$       | NaCl                      |
| $\text{NaHCO}_3$ and NaCl . . .   | E             | 0.09                   | 6.0                       |

Passing to systems with three solid phases, we have to decide which of the four possible combinations are capable of existence at a given temperature. We must consider the solubility of each salt in the reaction



and we can thus apply van 't Hoff's principle that the reciprocal pairs, i.e. the whole four salts, are capable of coexisting as separate solid phases only at that temperature at which the products of the concentrations are equal,

$$C_{\text{NaCl}} \times C_{\text{NH}_4\text{HCO}_3} = C_{\text{NH}_4\text{Cl}} \times C_{\text{NaHCO}_3}.$$

At this point there are six phases (four solid, one liquid, and one gaseous) in invariant equilibrium. At all other temperatures one of the two systems will change into its reciprocal; the one with the higher concentration-product will be unstable against the other. In the case of the ammonia-soda process we have always

$$C_{\text{NaCl}} \times C_{\text{NH}_4\text{HCO}_3} > C_{\text{NH}_4\text{Cl}} \times C_{\text{NaHCO}_3}.$$

Thus at  $0^\circ$ ,  $6.1 \times 1.5$  is greater than  $5.57 \times 0.82$ , and at  $30^\circ$   $6.1 \times 3.4$  is greater than  $7.78 \times 1.3$ . Thus NaCl and  $\text{NH}_4\text{HCO}_3$ ,



can never coexist at these temperatures, but only solutions saturated

- (1) with  $\text{NaHCO}_3 + \text{NH}_4\text{Cl} + \text{NH}_4\text{HCO}_3$  as solid phases, and  
 (2) with  $\text{NaHCO}_3 + \text{NH}_4\text{Cl} + \text{NaCl}$  as solid phases,

are capable of existence. The following values were found by Fedotieff for solutions saturated with the above two combinations of salts.

|                              | Solubility<br>at 0° | Solubility<br>at 15° |
|------------------------------|---------------------|----------------------|
| (1) $\text{NaHCO}_3$ ....    | 0.59                | 0.93                 |
| $\text{NaCl}$ .....          | 0.96                | 0.51                 |
| $\text{NH}_4\text{Cl}$ ..... | 4.92                | 6.28                 |
| (2) $\text{NaHCO}_3$ ....    | 0.12                | 0.18                 |
| $\text{NaCl}$ .....          | 4.83                | 4.44                 |
| $\text{NH}_4\text{Cl}$ ..... | 2.74                | 2.98                 |

On the isothermal evaporation of a saturated solution of two salts with a common ion, both salts separate out, but this is not always the case if the solution is saturated with three salts. This does happen with solution (2), since on isothermal evaporation the salts separate out which are present as solid phases, i.e.  $\text{NaHCO}_3$ ,  $\text{NaCl}$ , and  $\text{NH}_4\text{Cl}$ . But in the case of solution (1) we note a remarkable phenomenon. The solid phases are  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{HCO}_3$ , and  $\text{NH}_4\text{Cl}$ , yet, as the above table shows,  $\text{NaCl}$  appears in solution instead of  $\text{NH}_4\text{HCO}_3$ . Such solutions are termed by Meyerhofer "incongruent" saturated solutions, in contradistinction to "congruent" saturated solutions, which are distinguished by the fact that it is always possible by isothermal evaporation to obtain from them the same solid phases as those from which they were made up. From "incongruent" solutions, in which the liquid phase becomes of importance, another body can separate out than those which are present as solid phases. By isothermal evaporation "congruent" saturated solutions can be finally reached after a univariant equilibrium, but an "incongruent" saturated solution can never result from a "congruent" one. Thus we can add any quantity of solid  $\text{NH}_4\text{HCO}_3$  to solution (1) and the salt will remain unchanged, though quite small additions of solid  $\text{NaCl}$  change the composition of the solution, till with further amounts solution (1) turns

into solution (2). We have shown these points saturated with three salts as  $P_1$  and  $P_2$  in the projection diagram, by measuring off in our units along Oz the difference in the content in  $\text{NH}_4\text{Cl}$  and  $\text{NaHCO}_3$ , and then measuring the content in  $\text{NaCl}$  on a line at right angles to Oz. By the suitable combination of these two points with the points corresponding to saturation of two salts with a common ion, we obtain five more curves with the following meaning :—

|   |   |   |   |
|---|---|---|---|
| EP <sub>2</sub> , saturation with NaCl and NaHCO <sub>3</sub> |   |   |   |
| P <sub>2</sub> F  | „ | „ | NaCl and NH <sub>4</sub> Cl                             |
| P <sub>2</sub> P <sub>1</sub>                                 | „ | „ | NaHCO <sub>3</sub> and NH <sub>4</sub> Cl               |
| P <sub>1</sub> G  | „ | „ | NH <sub>4</sub> HCO <sub>3</sub> and NH <sub>4</sub> Cl |
| P <sub>1</sub> J  | „ | „ | NaHCO <sub>3</sub> and NH <sub>4</sub> HCO <sub>3</sub> |

These lines, and those of saturation by the separate salts, bound four surfaces which correspond to saturation with each salt in presence of two others, e.g. :—

|  |                                  |   |                    |
|--|----------------------------------|---|--------------------|
| Surface JDGP <sub>1</sub> , field of existence of (saturation with) NH <sub>4</sub> HCO <sub>3</sub> |                                  |   |                    |
| „  | P <sub>1</sub> GCFP <sub>2</sub> | „ | „                  |
| „  | FP <sub>2</sub> EB               | „ | „                  |
| „  | JAEP <sub>2</sub> P <sub>1</sub> | „ | „                  |
|  |                                  |   | NaHCO <sub>3</sub> |

The chief field of technical interest is that corresponding to solutions saturated with  $\text{NaHCO}_3$ , i.e. surface  $P_2P_1\text{JAE}$  and more particularly curves :—

|   |   |   |  |
|---|---|---|--|
| P <sub>1</sub> J, saturation with NaHCO <sub>3</sub> and NH <sub>4</sub> HCO <sub>3</sub> , |   |   |  |
| P <sub>2</sub> P <sub>1</sub>   | „ | „ | NaHCO <sub>3</sub> „ NH <sub>4</sub> Cl. |

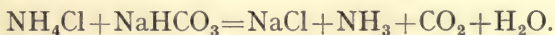
$P_1$  corresponds to an “incongruent” saturated solution, and thus  $\text{NaCl}$  appears in solution instead of  $\text{NH}_4\text{HCO}_3$  on the curve  $P_1\text{J}$  from the point of intersection with the  $\text{NH}_4\text{Cl}$  axis Oz up to the point  $P_1$ . The same holds for the curve  $P_2P_1$ .

Let us consider the influence of temperature on the field of existence of  $\text{NaHCO}_3$  (see numerical data above). The shift of the point  $P_1$  with temperature depends on the movement of the point J and mainly depends on the change in solubility of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HCO}_3$ . On raising the temperature further, to about  $32^\circ$ , the horizontal projection of the point  $P_1$  lies on the  $\text{NH}_4\text{Cl}$  axis. The “incongruent” saturated solution (r) thus becomes

a "congruent" saturated solution, since the same salts are now present in solution and as solid phases, i.e.  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_4\text{HCO}_3$ . We may now pass from a theoretical discussion to actual practice and consider the following questions:—

- (1) What are the factors on which the yield of solid  $\text{NaHCO}_3$  depends?
- (2) What is the influence of concentration?
- (3) What is the yield under given conditions?

Let us begin with brine and effect a double decomposition with  $\text{NH}_4\text{HCO}_3$ . It is obviously immaterial whether we take solid salt, or carbonate the ammoniacal brine. After the  $\text{NaHCO}_3$  has separated out, we have a solution of a certain content in  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NaHCO}_3$ . All the  $\text{NaHCO}_3$  left in solution is lost during the further treatment of the mother-liquor for the recovery of ammonia:—



It is convenient in practice to consider all the sodium in the mother-liquor as  $\text{NaCl}$ , and all the  $\text{NH}_3$  as being distributed between  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{Cl}$ . In the present case we can discuss the double decomposition from two sides:—

- (1) With respect to the amount of brine which is used up.
- (2) With respect to the amount of  $\text{NH}_3$  or  $\text{NH}_4\text{HCO}_3$  which is used up.

The coefficient of efficiency (i.e. the percentage used up) of

sodium  $U_{\text{Na}} = 100 \cdot \frac{\text{Cl} - \text{Na}}{\text{Cl}}$ , and that of ammonium  $U_{\text{NH}_4} =$

$100 \cdot \frac{(\text{NH}_4 - \text{HCO}_3)}{\text{NH}_4}$ , where the symbols represent grm. equivalents

per 1000 grms.  $\text{H}_2\text{O}$ . All the  $\text{Cl}$  and all the  $\text{Na}$  originally came into solution from  $\text{NaCl}$ , so that  $(\text{Cl} - \text{Na})$  is the sodium which separates out as solid phase. Thus the first formula gives the percentage of the sodium which separates out ( $\text{NaHCO}_3$ ). The second formula gives the percentage of the  $\text{HCO}_3$  separated out and also the percentage of ammonium effectively used, since the two are equivalent.

We will now consider our two solutions  $P_1$  and  $P_2$  and also solutions on the curves  $P_1P_2$  and  $P_1J$  which are saturated with only two salts. The following table gives the compositions:—

| No.  | Taken per<br>1000 grms. H <sub>2</sub> O |   | Solutions obtained grm.<br>equiv. per 1000 grms. H <sub>2</sub> O |      |      |                 | U Na % | U NH <sub>4</sub> % |
|--|--|---|---|------|------|-----------------|--------|---------------------|
|  | NaCl                                     | NH <sub>4</sub> HCO <sub>3</sub> /NH <sub>3</sub> | HCO <sub>3</sub>  | Cl   | Na   | NH <sub>4</sub> |        |                     |
| Solutions on the curve P <sub>2</sub> P <sub>1</sub> |  |   |   |      |      |                 |        |                     |
| P  | 479                                      | 295/63·4  | 0·18  | 8·17 | 4·62 | 3·73            | 43·4   | 95·1                |
| 1  | 448                                      | 360/77·5  | 0·31  | 7·65 | 3·39 | 4·56            | 55·7   | 93·4                |
| 2  | 417                                      | 431/92·7  | 0·51  | 7·13 | 2·19 | 5·45            | 69·2   | 90·5                |
| Solutions on the curve P <sub>1</sub> J              |  |   |   |      |      |                 |        |                     |
| P <sub>1</sub>                                       | 397                                      | 496/106·8   | 0·93  | 6·79 | 1·44 | 6·28            | 78·8   | 85·1                |
| 3  | 351                                      | 446/96·1  | 0·99  | 6·00 | 1·34 | 5·65            | 77·7   | 82·5                |
| 4  | 316                                      | 412/88·6  | 1·07  | 5·41 | 1·27 | 5·21            | 76·4   | 79·5                |
| 5  | 294                                      | 389/83·6  | 1·12  | 5·03 | 1·23 | 4·92            | 75·5   | 75·1                |
| 6  | 234                                      | 327/70·4  | 1·30  | 4·00 | 1·16 | 4·14            | 71·0   | 68·6                |

The numbers under NaCl and NH<sub>4</sub>HCO<sub>3</sub> give the amounts of these salts used in the double decomposition, while the next four columns give the concentrations of the respective ions in the solutions remaining after the separation of the solid.

The second numbers in column two give NH<sub>3</sub> in grms., since conclusions of considerable practical importance can be drawn from these numbers (Fedotieff). Let us begin with curve P<sub>2</sub>P<sub>1</sub>. We have here to compare four solutions, since P<sub>1</sub> lies on these curves as limiting point. As we have seen, the curve P<sub>2</sub>P<sub>1</sub> characterises solutions which are saturated with NaHCO<sub>3</sub> and NH<sub>4</sub>Cl. Examination of this curve will enable us to answer the following questions:—

- (1) How are we to operate to obtain a solution saturated with NH<sub>4</sub>Cl after the deposition of NaHCO<sub>3</sub>?
- (2) In this case, what influence does the molecular ratio between NaCl and NH<sub>4</sub>HCO<sub>3</sub> (or NH<sub>3</sub>) exert on the coefficient of efficiency of sodium and ammonium?

We see that solutions on the curve P<sub>2</sub>P<sub>1</sub> will be obtained in cases where there is a relatively very high excess of NaCl. The ratio NaCl:NH<sub>3</sub> changes from the point P<sub>2</sub> to the point P<sub>1</sub> as 2·2:1·7:1·3:1·1 (NH<sub>3</sub>=1).

The more the NaCl preponderates the more completely s



$\text{NH}_3$  used up ; at the point  $P_2$  95 per cent is used. On the other hand, the sodium is used up more completely the more  $\text{NaCl}$  is transformed into  $\text{NaHCO}_3$ , and this depends on the amount of  $\text{NH}_4\text{HCO}_3$ . However, this lowers the amount of  $\text{NH}_4\text{HCO}_3$  used up, i.e. more  $\text{NaHCO}_3$  remains in solution.

The curve  $P_1J$  characterises solutions saturated with  $\text{NaHCO}_3$  and  $\text{NH}_4\text{HCO}_3$ , and by examining it we find :—

- (1) How to operate so that after precipitation of  $\text{NaHCO}_3$  the remaining solution is saturated with  $\text{NH}_4\text{HCO}_3$ .
- (2) The influence of the ratio between  $\text{NaCl}$  and  $\text{NH}_4\text{HCO}_3$  in this case on the coefficient of efficiency.

We must first note here that the molar ratio only changes very slowly with considerable difference in the absolute amount to the same amount of water, thus (beginning from  $P_1$ ,  $\text{NH}_3=1$ )  $1.08 : 1.06 : 1.04 : 1.02 : 0.97$ .

While this does not affect the coefficient of efficiency of the  $\text{Na}$  very much it has a marked influence on that of the  $\text{NH}_3$ . Moving along  $P_1J$  from  $P_1$ , the coefficients of efficiency of both  $\text{Na}$  and  $\text{NH}_3$  diminish, and at the point of intersection with the  $\text{NH}_4\text{Cl}$  axis they are both equal to 75 per cent ; after this point the curve has no more technical interest. We note that  $U_{\text{Na}}$

(percentage of salt transformed to bicarbonate, of the whole amount taken) increases from  $J$  to  $P_1$ , where it attains a maximum and then gradually falls again. The decrease can be further followed on the curve  $P_2E$ .  $P_1$  is thus a maximum for the  $\text{NaCl}$  used up.  $U_{\text{NH}_4}$  gradually rises from  $J$  along the curves

$JP_1$ ,  $P_1P_2$ , and further on the curve  $P_2E$  (in the limit up to 100 per cent). The curve  $P_2E$  is of no practical importance. Common salt is a very cheap material, and it makes very little difference to the cost of the product whether more or less of it is used up. On the other hand,  $\text{NH}_3$  is comparatively dear, since although it is regenerated, each regeneration is accompanied by some loss. Thus from a manufacturing point of view it is important to use up the  $\text{NH}_3$  as completely as possible. Let us consider two solutions with about the same  $U_{\text{Na}}$ , e.g. No. 2 on

curve  $P_2P_1$  and No. 6 on  $P_1J$  (see table). In the former case, after deposition of solid  $\text{NaHCO}_3$ , 90.5 per cent of the  $\text{NH}_4\text{HCO}_3$  taken has been used up, but in the latter case only 68.6 per cent. From

this standpoint it is seen to be advisable to keep on the curve  $P_1P_2$ , where the coefficients of efficiency  $U_{NH_4}$  are high.

This has also been observed purely empirically. However, it is necessary to guard against using extreme excess of NaCl, since otherwise part of it will be thrown down. In fact, in the limit we reach the point  $P_2$ . When calcining the  $NaHCO_3$  a partial reaction then occurs with the deposited  $NH_4Cl$ , when NaCl is formed and the soda becomes less valuable.

On the other hand, if  $NH_3$  were cheap and NaCl dear we should rather keep on the curve  $P_1J$ .

We have now considered solutions saturated with two salts. However, in actual manufacture, solutions are usually obtained by carbonating ammoniacal solutions, saturated with NaCl, which are saturated with  $NaHCO_3$  alone. Such solutions are represented by the large surface  $P_1P_2EJ$ . In this case many different combinations are possible, and from purely practical reasons we will confine ourselves to ammoniacal solutions saturated with NaCl. We thus only consider solutions in which the consumption  $U_{NH_4}$  is not less than 75 per cent on the curve  $P_1J$  and the yield  $U_{Na}$  is not much below 70 per cent on the curve  $P_1P_2$ .

The dotted field shows the cases of practical importance. The nearer we approach  $P_1P_2$  the more complete is the consumption of  $NH_3$ . However, the nearer we approach  $P_2J$  the more complete is the consumption of NaCl. The following values for the point  $P_1$  show the influence of temperature :—

|                  | At 0° | At 15° | At 30° |
|------------------|-------|--------|--------|
| $U_{Na}$ .....   | 73·6  | 78·8   | 83·4   |
| $U_{NH_4}$ ..... | 88·0  | 85·1   | 84·1   |

Thus with rising temperature the yield of  $NaHCO_3$  and the consumption of ammonia rises. As we have said before, the constitution of solution No. 1 changes from 32° onwards by the NaCl content becoming smaller. For 32°

$$U_{Na} = U_{NH_4} = 84 \text{ \%}.$$

This is an optimum temperature for the yield of  $NaHCO_3$ .



|  | Solid   | Solubility in moles at 24.2° |                                 |                                |                   | Solubility in moles at 10° |                                 |                                |                   |
|--|---|------------------------------|---------------------------------|--------------------------------|-------------------|----------------------------|---------------------------------|--------------------------------|-------------------|
|  |   | 2NaNO <sub>3</sub>           | Na <sub>2</sub> CO <sub>3</sub> | K <sub>2</sub> CO <sub>3</sub> | 2KNO <sub>3</sub> | 2NaNO <sub>3</sub>         | Na <sub>2</sub> CO <sub>3</sub> | K <sub>2</sub> CO <sub>3</sub> | 2KNO <sub>3</sub> |
| Solutions saturated with one salt and with two salts | NaNO <sub>3</sub> alone   | 5.37                         | —                               | —                              | —                 | 4.730                      | —                               | —                              | —                 |
|  | NaNO <sub>3</sub><br>Na <sub>2</sub> CO <sub>3</sub> , 7H <sub>2</sub> O                                    | 3.69                         | 2.05                            | —                              | —                 | 4.167                      | 0.8247*                         | —                              | —                 |
|  | Na <sub>2</sub> CO <sub>3</sub> , 7H <sub>2</sub> O<br>Na <sub>2</sub> CO <sub>3</sub> , 10H <sub>2</sub> O | 2.701                        | 2.482                           | —                              | —                 | separates out at 10°       |                                 |                                | —                 |
|  | Na <sub>2</sub> CO <sub>3</sub> , 10H <sub>2</sub> O<br>alone   | —                            | 2.691                           | —                              | —                 | —                          | 1.129                           | —                              | —                 |
|  | Na <sub>2</sub> CO <sub>3</sub><br>double salt  | —                            | 3.422                           | 1.760                          | —                 | —                          | 1.663                           | 2.561                          | —                 |
|  | K <sub>2</sub> CO <sub>3</sub><br>double salt   | —                            | 1.06                            | 7.77                           | —                 | —                          | 0.5767                          | 7.61                           | —                 |
|  | K <sub>2</sub> CO <sub>3</sub> alone  | —                            | —                               | —                              | —                 | —                          | —                               | 7.838                          | —                 |
|  | K <sub>2</sub> CO <sub>3</sub> + KNO <sub>3</sub>   | —                            | —                               | 8.040                          | 0.153             | —                          | —                               | 7.780                          | 0.1316            |
|  | KNO <sub>3</sub> alone  | —                            | —                               | —                              | 1.86              | —                          | —                               | —                              | 1.49              |
|  | NaNO <sub>3</sub> + KNO <sub>3</sub>  | 5.95                         | —                               | —                              | 2.15              | 4.949                      | —                               | —                              | 1.49              |
| Solutions saturated with three salts                 | NaNO <sub>3</sub><br>Na <sub>2</sub> CO <sub>3</sub><br>KNO <sub>3</sub>                                    | 4.165                        | 2.055                           | —                              | 1.400             | 4.479                      | 0.619                           | —                              | 1.06              |
|  | KNO <sub>3</sub><br>Na <sub>2</sub> CO <sub>3</sub><br>double salt  | —                            | 3.695                           | 0.184                          | 1.053             | —                          | 1.513                           | 0.1334                         | 0.707             |
|  | K <sub>2</sub> CO <sub>3</sub><br>KNO <sub>3</sub><br>double salt   | —                            | 0.734                           | 7.338                          | 0.312             | —                          | 0.4981                          | 7.408                          | 0.0715            |

\* Na<sub>2</sub>CO<sub>3</sub> is always present with 10H<sub>2</sub>O in the solid phase at 10°.



Firstly, the two alkali carbonates furnish a double salt,  $\text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, 6\text{H}_2\text{O}$ . Thus we obtain two points, U and T, saturated with carbonates, corresponding to saturation with  $\text{Na}_2\text{CO}_3$  and double salt, and with  $\text{K}_2\text{CO}_3$  and double salt. Owing to the occurrence of the double salt there are three solutions saturated with three salts:—

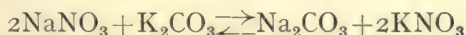
|         |                 |                  |                   |   |
|---------|-----------------|------------------|-------------------|---|
| $P_1$ , | saturation with | $\text{KNO}_3$ , | $\text{NaNO}_3$ , | $\text{Na}_2\text{CO}_3$ .              |
| $P_2$ , | „               | „                | $\text{KNO}_3$ ,  | double salt, $\text{Na}_2\text{CO}_3$ . |
| $P_3$ , | „               | „                | $\text{KNO}_3$ ,  | „ „ $\text{K}_2\text{CO}_3$ .           |

Further, we have the four fields of existence of the four salts composing the system:  $\text{KNO}_3$  ( $\text{RBSP}_3\text{P}_2\text{P}_1$ ),  $\text{K}_2\text{CO}_3$  ( $\text{SCTP}_3$ ),  $\text{NaNO}_3$  ( $\text{RAQ}_1\text{P}_1$ ), and  $\text{Na}_2\text{CO}_3$  ( $\text{P}_1\text{Q}_1\text{Q}_2\text{DUP}_2$ ), and also the field of the double salt ( $\text{UTP}_3\text{P}_2$ ).

With respect to the  $\text{Na}_2\text{CO}_3$  field we must note that, at  $10^\circ$ ,  $\text{Na}_2\text{CO}_3$  is present in the whole  $\text{Na}_2\text{CO}_3$  field with  $10\text{H}_2\text{O}$ , but that at  $24.2^\circ$  the field is divided into three fields:—

|     |                                  |   |                 |
|-----|----------------------------------|---|-----------------|
|     | $\text{Q}_2\text{DUq}$ with      | $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$  | as solid phase, |
|     | $\text{Q}_2\text{Q}_1\text{rsq}$ | „ $\text{Na}_2\text{CO}_3, 7\text{H}_2\text{O}$ | „ „             |
| and | $\text{rsP}_2\text{P}_1$         | „ $\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$  | „ „             |

Thus along  $\text{P}_1\text{P}_2$  there is a solution saturated with  $\text{KNO}_3$  and with  $\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$ . We may note finally that the two salts  $\text{KNO}_3$  and  $\text{NaNO}_3$ , with a common ion, do not mutually lower their solubilities, but raise them. The formation of a double salt in the solid state has not been observed in crystallisation from the solutions and thus the phenomenon must be ascribed to the existence of complex ions. After this theoretical discussion of the system



we may consider the practical aspect of the reaction.

Let us bring  $\text{NaNO}_3$  and  $\text{K}_2\text{CO}_3$  together in suitable amounts and at suitable concentration, as is done in practice.  $\text{KNO}_3$  is precipitated, and after it has separated out in the solid state a solution is left which is saturated with  $\text{KNO}_3$  and contains two other salts in solution. We will first choose  $24.2^\circ$  as the temperature of precipitation. A solution will be obtained which corresponds with some point on the field of existence of  $\text{KNO}_3$  ( $\text{RP}_3\text{P}_2\text{P}_1\text{SB}$ ): the position of this point will be determined by the concentrations of the  $\text{NaNO}_3$  and  $\text{K}_2\text{CO}_3$  taken. The con-



$P_1P_2$  (saturation with both  $Na_2CO_3$  and  $KNO_3$ ). We will now calculate the coefficients  $U_K$  and  $U_{Na}$  which correspond to the solutions  $P_1$  and  $P_2$ . The following table shows that the coefficients for the two initial substances at the point  $P_2$  (saturation with  $Na_2CO_3$ ,  $KNO_3$ , and double salt) are better than at the point  $P_1$  (saturation with  $Na_2CO_3$ ,  $NaNO_3$ , and  $KNO_3$ ):—

| Temperature of experiment | Point              | Solubility in 1000 grms. water |           |          |         | Solubility in 1000 grms. water |       |            |        | $U_K$ | $U_{Na}$ |
|---------------------------|--------------------|--------------------------------|-----------|----------|---------|--------------------------------|-------|------------|--------|-------|----------|
|                           |                    | $Na_2CO_3$                     | $K_2CO_3$ | $NaNO_3$ | $KNO_3$ | $Na_2$                         | $K_2$ | $(NO_3)_2$ | $CO_3$ |       |          |
| 24.2°                     | $P_1$              | 21.7                           | —         | 709      | 282     | 6.22                           | 1.40  | 5.68       | 2.05   | 31.7  | 8.6      |
|                           | Point on $P_1P_2$  | 37.6                           | —         | 25       | 235     | 3.69                           | 1.17  | 1.31       | 3.55   | 67.1  | 64.5     |
|                           | $P_2$              | 37.7                           | 2         | —        | 232     | 3.57                           | 1.15  | 1.14       | 3.55   | 67.6  | 68.0     |
|                           | Point near $P_2^*$ | 37.8                           | —         | 64       | 382     | 3.96                           | 1.90  | 2.27       | 3.57   | 46.8  | 30.3     |
|                           | $P_3$              | 77.87                          | 101.49    | —        | 3154    | 0.74                           | 7.52  | 0.16       | 8.07   | 6.8   | 78.4     |
| 10°                       | $P_2'$             | 160.6                          | 18.46     | —        | 142.8   | 1.61                           | 0.91  | 0.74       | 1.77   | 48.6  | 54.0     |

\* Only saturated with  $KNO_3$ .

Thus a solution saturated with  $KNO_3$  whose composition is near  $P_2$  gives a less efficient consumption of the two initial substances.

The maximum efficiency is clearly at the point  $P_2$ , for towards  $P_3$  the coefficient for potassium is again less, as shown by the table, and such a solution is of no importance in practice. If we take 29.5 grms.  $NaNO_3$ , 24.5  $K_2CO_3$ , and 50 water, so that the solution will correspond to the point  $P_2$  after precipitation, we obtain 24.1 dry substance which is contaminated with 4.5 per cent carbonate. Allowing for this, the amount of pure  $KNO_3$  is



23.0 grms., while theory requires 23.6. The relatively high carbonate content is due to the fact that it is more difficult to press out the mother-liquor when working on the small scale than in a factory, where presses are employed.

Sodium carbonate can be easily obtained by adding  $\text{NaNO}_3$  to the mother-liquor at the point  $P_2$ , after precipitation of  $\text{KNO}_3$ . We then move away from  $P_2$  towards  $P_1$  along the line  $P_2P_1$  of saturation with  $\text{KNO}_3$  and  $\text{Na}_2\text{CO}_3$ . At  $P_2$  there is practically no  $\text{NaNO}_3$  in solution; the addition of this salt lowers the solubility of  $\text{Na}_2\text{CO}_3$  and therefore precipitates it; the solubility of  $\text{Na}_2\text{CO}_3$  is 37.7 grms. per lit. at  $P_2$ , but only 21.7 at  $P_1$ .

$\text{KNO}_3$  cannot separate, since its solubility rises towards  $P_1$ . To obtain a solution corresponding to  $P_1$  after precipitation of soda, we have to add  $\text{K}_2\text{CO}_3$ , which reacts with the  $\text{NaNO}_3$  now present in large excess, forming  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ .  $\text{Na}_2\text{CO}_3$  is precipitated and  $\text{K}_2\text{CO}_3$  remains in solution, causing the solution to be saturated with  $\text{KNO}_3$ . 70 grms. (=46 water + 24 solid) of the mother-liquor remaining after precipitation of  $\text{KNO}_3$  were treated with  $\text{NaNO}_3$ . The difference in composition between solutions  $P_2$  and  $P_1$  per 1000 c.c. water is:—

With respect to  $\text{NO}_3=562$  grms.  $\text{NO}_3$  (=77.0  $\text{NaNO}_3$  per 100 grms. water).

With respect to  $\text{K}=20$  grms.  $\text{K}$  (=1.37  $\text{K}_2\text{CO}_3$  per 100 grms. water).

This corresponds to 35.4  $\text{NaNO}_3$  and 0.6  $\text{K}_2\text{CO}_3$  per 46 water. These amounts of the solid salts were therefore added to the 70 grms. of solution. The difference in the solubility of  $\text{Na}_2\text{CO}_3$  at the points  $P_2$ ,  $P_1$  is 160 grms. per lit., i.e. 7.36 for 46 grms. water. This is the theoretical yield of the process. The sodium carbonate separating along  $P_1P_2$  contains 1  $\text{H}_2\text{O}$ , and thus 7.36 grms. soda will remove 1.25 grms. from the solution. This loss was covered by the addition of 1.25 grms. water to the solution, which was then shaken for about one day. The experiment gave 7.07 grms. anhydrous soda (99.1 per cent pure), which is in excellent agreement with the calculated yield.

We will now consider the influence of temperature on the practical working of the reaction, i.e. when the precipitated salt is filtered at  $10^\circ$  instead of at  $24.2^\circ$ . We again start from  $P_2$  (saturation with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{KNO}_3$ ) at  $24.2^\circ$ ; we



have seen that the coefficient for potassium is very good at this temperature. Referring to the last row in the table ( $P'_2$ ) we see that at  $10^\circ$  the coefficients for both initial substances are smaller than at  $24.2^\circ$ , from which we may conclude that it would be better in practice to filter at a higher temperature, e.g.  $25^\circ$ . A small technical experiment was made at  $10^\circ$ . 12.2 grms.  $K_2CO_3$  and 14.7  $NaNO_3$  were shaken with 50 c.c. water at  $10^\circ$ , in order to obtain, after precipitation of  $KNO_3$ , a solution  $P'_2$  (analogous to  $P_2$ ). The yield was 8.6 grms.  $KNO_3$ . 12.2 grms.  $K_2CO_3$  are equivalent to 17.9  $KNO_3$ , and as the coefficient is 48.6 per cent the theoretical yield is 8.68 grms.  $KNO_3$ . The agreement is thus very good.

To obtain soda from the mother-liquor we must again move on to the line of saturation with  $Na_2CO_3$ ,  $NaNO_3$ , and  $KNO_3$ . We can do this by adding  $NaNO_3$  and a small quantity of  $K_2CO_3$  to cover the difference in solubility of  $KNO_3$  at the points  $P'_2$  and  $P'_1$ . The calculated amounts, 41.7 grms.  $NaNO_3$  and 1.5  $K_2CO_3$ , were added to the mother-liquor (=50 grms. water). The difference between the solubility of  $Na_2CO_3$  at the points  $P'_2$  and  $P'_1$  is 95.1 grms. per lit. water. Thus 4.76 grms.  $Na_2CO_3$ \* should be separated from a solution containing 50 grms. water on passing from the point  $P'_2$  to  $P'_1$ . However, at  $10^\circ$   $Na_2CO_3$  separates out with 10  $H_2O$  along the line  $P'_1P'_2$  (saturation with  $Na_2CO_3$  and  $KNO_3$ ). Since theoretically 4.76 grms.  $Na_2CO_3$  will be precipitated, and since at  $10^\circ$  the crystals contain 10  $H_2O$ , 8.1 grms. water will be removed from the solution. In order to cover this loss 8.1 grms. water were added, together with the 41.7 grms.  $NaNO_3$  and 1.5  $K_2CO_3$ . After shaking for about one day, a precipitate was obtained which weighed 5.00 grms. when dry and contained 96.0 % = 4.8 grms.  $Na_2CO_3$ , which is in excellent agreement with the theoretical yield, 4.76 grms.

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\* Obviously this relates to anhydrous  $Na_2CO_3$ .



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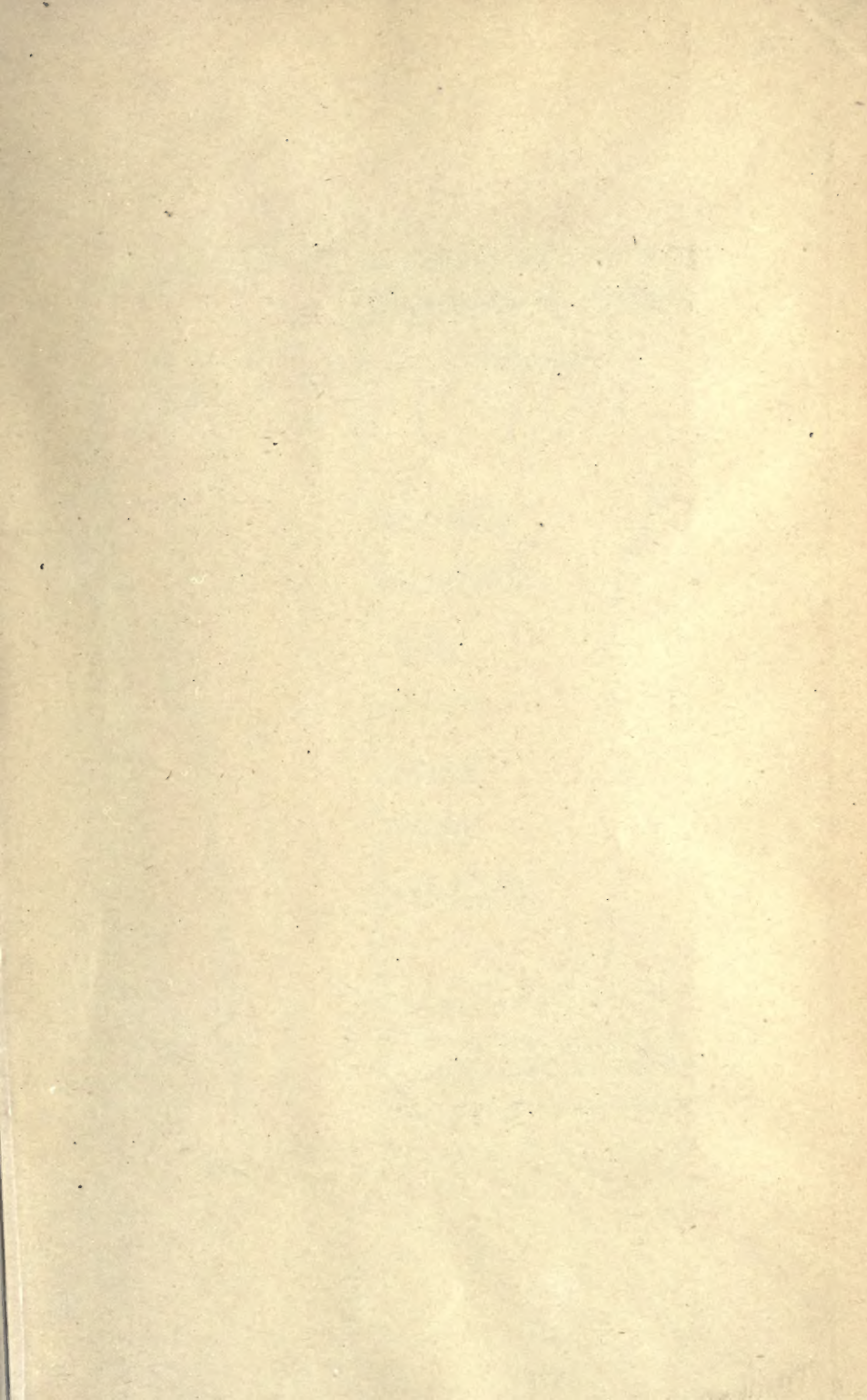
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